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# INVESTIGATION OF WATER-SOLUBLE CHEMILUMINESCENT MATERIALS

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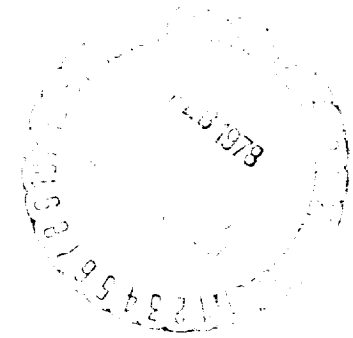

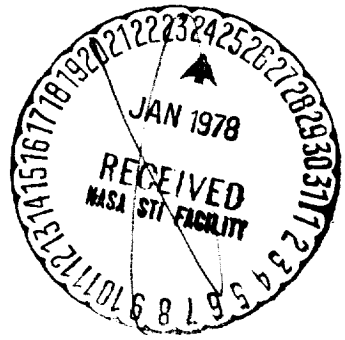

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16. Abstract

The feasibility of water-initiated peroxyoxalate chemiluminescence has been established. A mixture of Rhodamine B, a sulfonamido substituted dichlorophenyl oxalate and a solid hydrogen peroxide source, sodium perborate, provides emission for about 15 minutes on contact with water. Structural criteria for optimum water-soluble oxalate esters and fluorescers have been obtained. The feasibility of a rain-activated chemiluminescent highway strip is now established.

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## SUMMARY AND CONCLUSIONS

The feasibility of employing a rain-activated chemiluminescent system to delineate wet highway traffic lanes at night has been investigated. The initial phase of the program, described in this report, has demonstrated that oxalic ester chemiluminescence, which is the only efficient chemiluminescent reaction known, can be modified to generate light under aqueous conditions. Oxalic ester chemiluminescence had previously been restricted to organic solvent systems.

The most efficient water-activated system found during this phase involves reaction of a sulfonamide substituted dichlorophenyl ester of oxalic acid with sodium perborate in the presence of Rhodamine B. Addition of water to a mixture of the solid reactants produces a moderate intensity, orange-red light emission which lasts for about 15 minutes. The orange-red emission is characteristic of the fluorescence spectrum of Rhodamine B.

While the results of this investigation establish feasibility for aqueous oxalic ester chemiluminescence, the efficiencies of the reactions discovered are inadequate to meet the brightness-lifetime requirements of highway traffic lane delineation. It is believed on the basis of the results, however, that high efficiency oxalates and fluorescers for aqueous chemiluminescence are possible and that superior systems meeting the requirements can be developed.

## INTRODUCTION

The delineation of highway traffic lanes under rainy conditions at night is a serious problem particularly in areas where raised reflectors cannot be used due to frequent snow-plowing. A study on the feasibility of a self-luminous marking system was carried out[1] and the conclusion was that a rain-activated chemiluminescent system was a possible solution to the rainy-nighttime delineation problem.

The peroxy-oxalate chemiluminescent system is the most efficient nonbiological chemiluminescent reaction known[2]. In addition, it is the only practical chemical lighting system in commercial use today.

The attractive practical potential of oxalate ester chemiluminescence is based on:

(1) A high theoretical light energy density of 173,000 lm. hr. $l^{-1}$ equivalent to the light output of a 40-watt incandescent bulb burning continuously for 2 weeks. This high energy density makes chemiluminescence especially suited for portable lighting applications and for other applications where the use of distributed power is inconvenient or impossible.

(2) Chemiluminescence is cold light. Since heat and flame are absent, chemiluminescent systems can be used where conventional hot lights would cause fire or explosion. Automobile and aircraft accidents, coal mines, repair of gas transmission lines are examples.

(3) Reliability through long shelf life. Conventional battery systems gradually lose energy even when in storage. Chemiluminescent systems, in principle, can have indefinite storage lifetimes.

The current oxalic ester system utilizes an organic solvent which constitutes most of its weight and volume. A substantial increase in practical efficiency (ie, light output per unit weight and volume) could be obtained through development of a solid state formulation, comprised primarily of active ingredients. The formulation would be activated by water provided independently at the point of use. This solid state formulation would be particularly well suited to serve as the basis for a highway marking system useful under rainy conditions at night, but would also serve other uses where portability or limited storage space requirements are critical.

The objective of this research program was the development of an oxalate ester chemiluminescent system capable of high light capacity in aqueous solution. Attainment of this initial goal would then be followed by formulation of the active ingredients into a water-activated system suitable for demonstrating the feasibility of the rain-activated self-luminescent highway stripe.

## RESULTS AND DISCUSSION

### I. FUNDAMENTAL CONCEPTS

Oxalate ester chemiluminescence can be summarized by the following reaction sequence[2,3,4]:

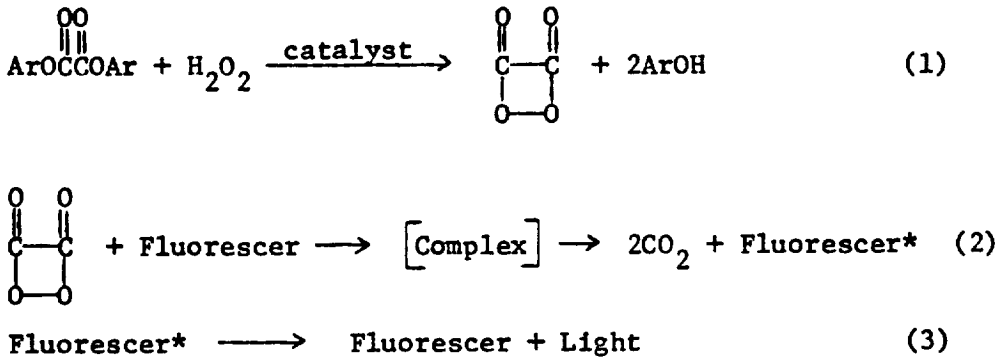



Figure 1. Mechanism of Oxalate Ester Chemiluminescence

Ar is an electronegatively substituted phenyl ring such as 2,4,6-trichlorophenyl, 2,4-dinitrophenyl or 2,4,5-trichloro-6-carbopentoxyphenyl, and * indicates an electronically excited state. The initial reaction is a base catalyzed nucleophilic substitution process providing a key chemiluminescent intermediate believed to be 1,2-dioxetandione (eq. 1). The decomposition of the key intermediate to carbon dioxide provides sufficient energy to excite a fluorescent molecule to the first excited singlet state (eq. 2) which then emits radiation in a conventional fluorescence process (eq. 3). The current practical oxalate ester chemiluminescent formulations employ organic solvents containing oxalate esters and fluorescers which are insoluble in water. Successful demonstration of a fully aqueous system requires structural modification of both the fluorescer and the oxalate ester. Thus, the initial research effort was directed towards the design and synthesis of water-soluble oxalate esters and fluorescers which are expected on the basis of efficiency criteria established in earlier research programs[4a-4c] to provide chemiluminescence when treated with hydrogen peroxide. These two aspects of the synthetic program are treated in separate sections (II and III) below.

## II. OXALATE ESTER DESIGN AND SYNTHESIS

### A. Structure-Efficiency Correlation

A potential problem in design of efficient oxalate esters is the fact that water and hydroxide ion are both nucleophiles and in principle could compete with hydrogen peroxide (probably attacking as the $OOH^-$ ion) in the initial step of attack by the nucleophile on the oxalate carbonyl group. However, the relative nucleophilic reactivity of the peroxide anion versus water or hydroxide ion strongly favors preferential attack by $OOH^-$ in aqueous systems. In some recent work Ritchie[5] has correlated the reactivities of a large number of nucleophiles and clearly confirmed Jencks'[6] conclusion that attack by $OOH^-$ on an ester is strongly favored over water and hydroxide ion.

Oxalate esters which exhibit high efficiency in the peroxyoxalate chemiluminescent system are, in general, highly reactive towards hydrogen peroxide. Most of these esters are phenyl oxalates which contain several electron attracting substituents which facilitate the displacement of the phenoxide ion when the ester is attacked by hydrogen peroxide. A quantitative correlation of the electron-attracting power of the substituents, as measured by the sum of the Hammett sigma constants, with the efficiency of the nonaqueous chemiluminescent reaction was attempted using data which was obtained from earlier work[4a-e]. Data were limited to those in which BPEA was employed as the fluorescer so that variations in the excitation and emission steps of the reaction could be minimized. The data are summarized in Table 1 and expressed graphically in Figure 2. The fit to a linear correlation was poor*, but results show that the efficient oxalate esters generally have $\Sigma\sigma$ which fall in the range 1.6 to 2.5. The poor correlation is not surprising since there are factors other than the ease of displacement which effect the overall efficiency. Chemical and fluorescence quenching by the oxalate ester are examples of such efficiency reducing processes. The $\Sigma\sigma$ correlation is useful, however, in eliminating oxalate structures which have a low probability of giving a highly efficient chemiluminescent reaction.

*The linear regression method is outlined in Appendix II.

Table 1. Effect of oxalate structure on chemiluminescent performance.

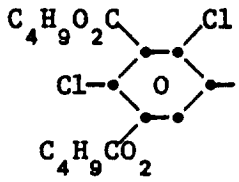
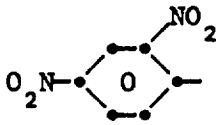
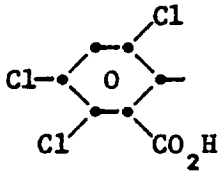
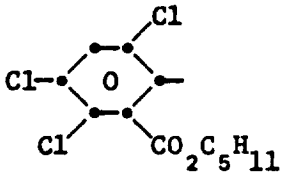
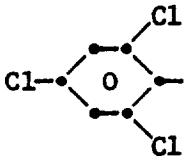
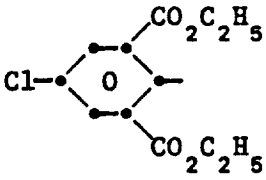
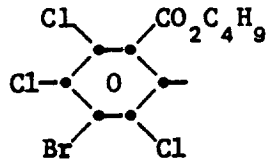
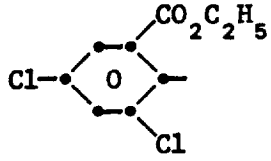
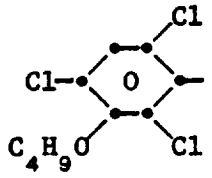
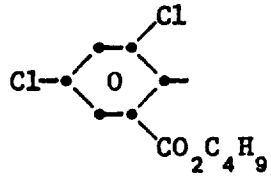
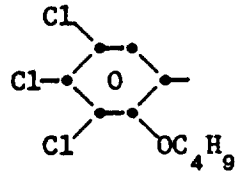
| ArOCCOAr<br>Ar = | Conc. M | Solvent[a] | $QY^b$ x$10^2$ | $\Sigma\sigma^c$ | Reference |
|---|---|---|---|---|---|
| A.  | 0.01 | 75-DBP<br>25-3MP | 15.2 | 1.65 | 4b |
| B.  | 0.10 | 100 DMP | 15.1 | 2.48 | 4a |
| C.  | 0.10 | 80-DEC<br>20-3MP | 10.7 | 1.98 | 4b |
| D.  | 0.10 | 75-DBP<br>25-3MP | 9.06 | 2.02 | 4b |
| E.  | 0.03 | 90-EB<br>10-TBA | 8.70 | 1.63 | 4b |
| F.  | 0.01 | 75-DBP<br>20-DMP<br>5-TBA | 6.50 | 1.67 | 4c |

Table 1. Effect of oxalate structure on chemiluminescent performance. (Continued)

| ArOCCOAr<br>Ar = | Conc.<br>M | Solvent[a] | $QY^b$ x$10^2$ | $\Sigma\sigma^c$ | Reference |
|---|---|---|---|---|---|
| G.  | 0.10 | 75-EB<br>25-3MP | 5.92 | 2.37 | 4b |
| H.  | 0.10 | 75-EB<br>25-3MP | 2.04 | 1.61 | 4b |
| I.  | 0.10 | 75-EB<br>25-3MP | 1.34 | 1.71 | 4b |
| J.  | 0.10 | 75-EB<br>25-3MP | 1.03 | 1.61 | 4b |
| K.  | 0.10 | 75-DBP<br>25-3MP | 0.71 | 0.97 | 4b |

[a]Values given indicate the percent by volume of each solvent. DBP is dibutyl phthalate, DMP is dimethyl phthalate, DEC is diethyl carbitol, 3MP is 3-methyl-3-pentanol, EB is ethyl benzoate, and TBA is tert-butanol.

[b]Chemiluminescence quantum yield in Einstein $mole^{-1}$.

[c]The sum of the Hammett sigma values. Sigma values were taken principally from Ritchie and Sager[7] and Barlin and Perrin[8].

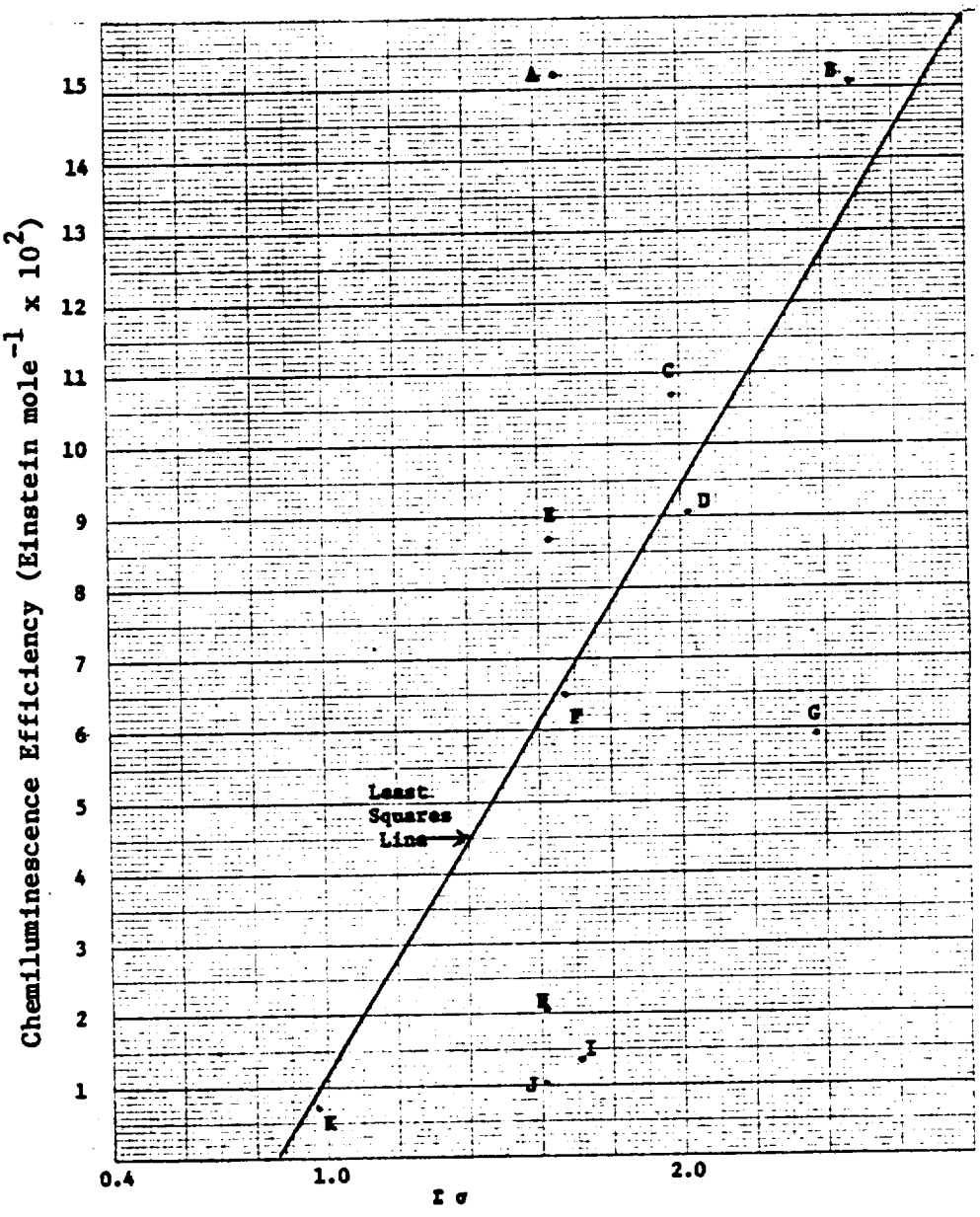
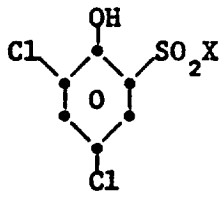



Figure 2. Correlation of chemiluminescence efficiency with sum of Hammett sigma values.

## B. Synthesis of New Oxalate Esters

### 1. Sulfonamide Derivatives

A series of oxalate esters was prepared from the phenols of general formula 1.



1

a. X = Cl

b. X = $N(CH_2CH_2)_2O$

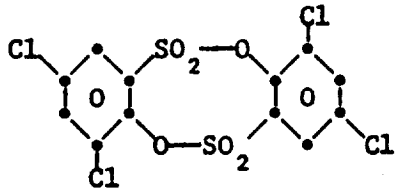
c. X = $N(CH_2CH_2OCH_3)_2$

d. X = $N(CH_2CH_3)CH_2CH_2N(CH_2CH_3)_2$

e. X = $N(CH_2CH_3)CH_2CH_2\overset{+}{N}CH_3(CH_2CH_3)_2$

The sulfonamides 1b, c and e were selected because the oxalate esters derived from these compounds were expected to have the desired water solubility and the $\Sigma\sigma$ was calculated to be 1.63. In addition, the sulfonyl chloride, 1a, is available commercially.

In the initial attempts to prepare 1c, a high melting by-product was formed and subsequently identified by mass spectra and elemental analysis as the cyclic anhydride 2. This compound is probably formed

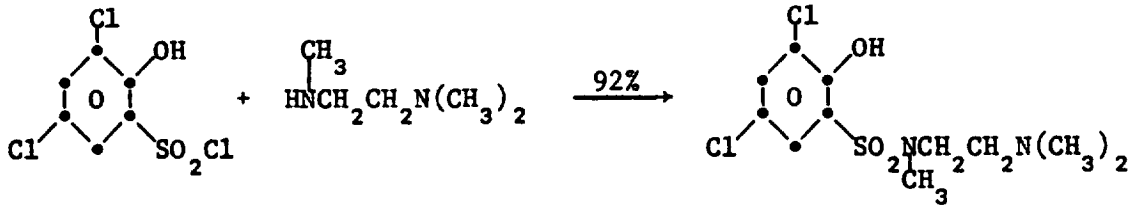


2 mp 311.5-312.5

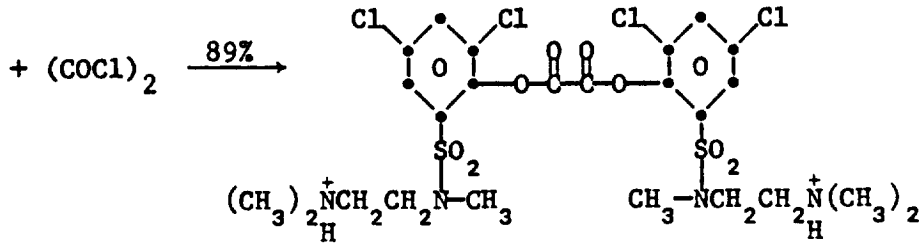
by a base promoted dimerization of the sulfonyl chloride. It was shown that this material could be produced in 49% yield by stirring with an excess of triethylamine at room temperature. Formation of 2 was virtually eliminated in subsequent aminations of 1a by adding the sulfonyl chloride slowly to the amine so that the concentration of sulfonyl chloride is kept low enough to avoid the dimerization and favor the sulfonamide formation.

Oxalate esters were successfully prepared from the sulfonamides 1b and 1c but the water solubility of these compounds was minimal and therefore these compounds were not evaluated in the aqueous reaction.

The presence of the tertiary amino group in sulfonamide 1d presented a difficult problem because the liberation of the tertiary amine from the product of the oxalyl chloride reaction, a hydrochloride salt, requires a base which will neutralize the HCl yet not attack the oxalate carbonyl group. Treatment of 1d with oxalyl chloride gave a solid whose infrared spectrum indicated the presence of the oxalate carbonyl, but nmr and elemental analysis were not consistent with the expected structure, the dihydrochloride salt of the oxalate ester. The product from the oxalyl chloride reaction was treated with potassium tert-butoxide, a strong base but a poor nucleophile, in an attempt to liberate the tertiary amine. Methyl triflate ($CH_3OSO_2CF_3$), a powerful methylating reagent, was added to the crude product in an effort to prepare the quaternary ammonium salt. Once again nmr did not confirm the expected structure. Qualitative chemiluminescence tests on aqueous solutions of these two products with hydrogen peroxide and a fluorescer such as disulfoperylene gave a detectable emission with the lifetime of the "alkylated" product being of the order of 5 to 10 minutes and the unalkylated product being 30 seconds to 1 minute. The structure of the compound which gave the chemiluminescent reaction was uncertain. Since the nmr of the active compounds was complicated by the presence of several ethyl groups and the water solubility was low, it was decided to prepare the corresponding methyl analog so that the methyl groups would appear as singlets in the nmr and the water solubility improved. The oxalate ester was prepared from the commercially available sulfonyl chloride 1a as shown on page 9.

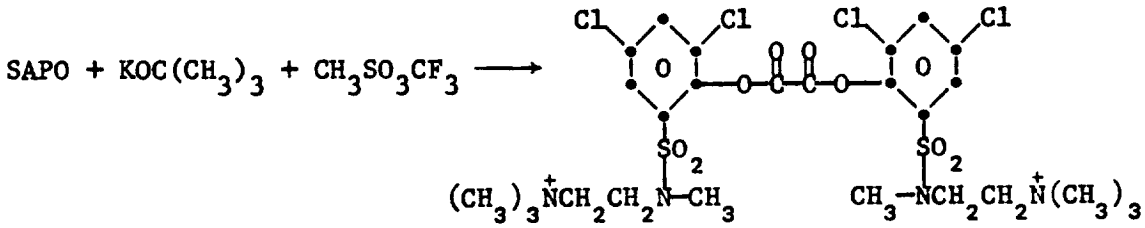


1a 3



2 $Cl^-$

4 SAPO

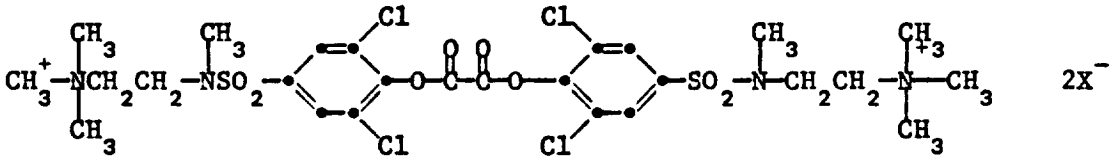


5 2 $\bar{O}_3SCF_3$

The nmr spectra of 3, SAPO and 5 were consistent with the appropriate structures showing the various methyl groups as distinct singlets. The ir spectra of SAPO and 5 showed the oxalate carbonyl near 1800 $cm^{-1}$.

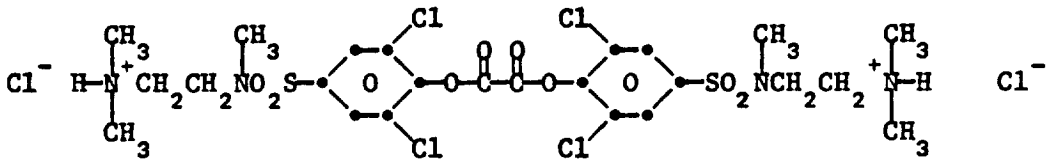
Qualitative chemiluminescent tests on SAPO and 5 demonstrated a bright chemiluminescent emission from both compounds in aqueous media, but a longer-lived emission was evident from SAPO. This represented the initial example of a fully aqueous oxalate ester chemiluminescent reaction. Details of the formulation of SAPO into a water-activated system are described in Section IV.

Because of the success with SAPO, a related compound, PAPO, was prepared in an attempt to improve the reactivity and solubility properties of SAPO. The sulfonyl chloride of 2,6-dichlorophenol was



PAPO

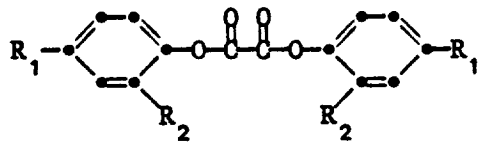
prepared in 93% crude yield by treatment of the phenol with chlorosulfonic acid. Recrystallization afforded the pure material in 80% overall yield. Reaction of this sulfonyl chloride with N,N,N'-trimethylethylene diamine presented some difficulty due to base promoted polymerization of the acid chloride. This side-reaction was circumvented by extremely slow addition of the sulfonyl chloride via a syringe pump. This minimized the instantaneous concentration of sulfonyl chloride and therefore suppressed the polymerization reaction. Treatment of this phenol with oxalyl chloride afforded the hydrochloride salt 6 which gave the brightest aqueous chemiluminescent reaction



6

observed thus far. However, the lifetime of this emission was very short due to the rapid hydrolysis of this oxalate since no emission was detected when hydrogen peroxide was added to a solution of 6 in water which had been prepared a few minutes before.

The high reactivity of the sulfonamido-substituted oxalate ester SAPO prompted us to consider less reactive analogs. The monochlorophenyl derivatives 7a and 7b were selected as candidates, since their reactivity towards nucleophilic attack by $H_2O_2$ should be substantially lower than the reactivity of 6 ($\Sigma\sigma = 1.93$).



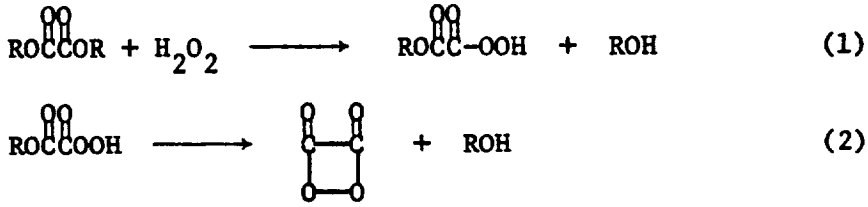
7a. $R_1 = SO_2N(CH_3)CH_2CH_2\overset{+}{N}H(CH_3)_2\ \ Cl^-$; $R_2 = Cl$ ($\Sigma\sigma = 1.25$)

b. $R_1 = Cl$; $R_2 = SO_2N(CH_3)CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$

The key intermediates for the synthesis of 7a and 7b are the respective sulfonyl chlorides, 3-chloro-4-hydroxybenzene sulfonyl chloride and 2-hydroxy-5-chlorobenzene sulfonyl chloride. In spite of the ease of preparing the corresponding dichloro derivatives, satisfactory methods for the preparation of working quantities of these sulfonyl chlorides could not be developed, even though literature methods were employed and a large number of experimental variations were investigated. Work in this area was suspended in favor of syntheses with higher probabilities of success.

## 2. Aromatic Quaternary Ammonium Compounds

The primary requirements for chemiluminescent efficiency in an oxalate ester is the ability of the alcohol portion of the ester to be displaced by hydrogen peroxide (eq. 1) and to cyclize rapidly by

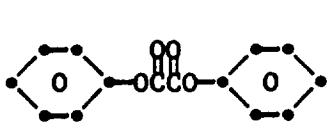


(1)



(2)

displacement of a second molecule of alcohol (eq. 2). In a diaryl oxalate the ability of the phenol to be displaced is greatly enhanced by the presence of electron attracting substituents on the aromatic ring. For example, diphenyl oxalate (8) does not give appreciable light



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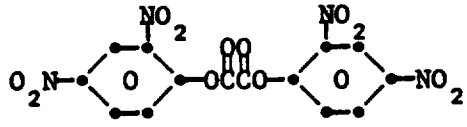
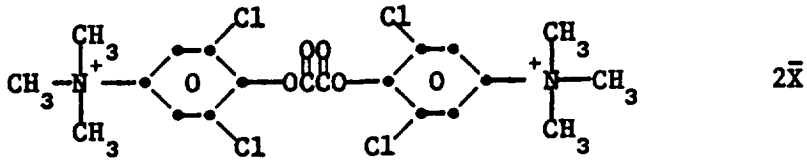


9

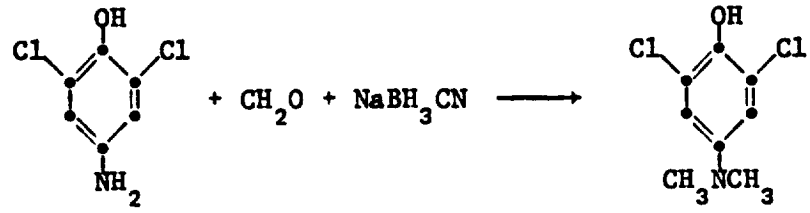
emission on treatment with hydrogen peroxide in the presence of a fluorescer. Substitution of two strongly electron-attracting substituents such as nitro groups on the aromatic rings as in 9 increases the reactivity towards hydrogen peroxide so that appreciable chemiluminescent emission is now observed. In Section II A of this report, a correlation between the chemiluminescent efficiency and the electron density of the aromatic ring was attempted. The electron density was assumed to be related to the sum of the Hammett sigma constants, $\Sigma\sigma$. Although the correlation was only qualitative, the results did indicate that the most efficient oxalate esters had $\Sigma\sigma$ values in the range of 1.6 to 2.5. Applying this guideline to potentially water-soluble oxalates, compound 10 was selected as a prime candidate for synthesis. The electron density



10 $\Sigma\sigma = 2.18$

of the aromatic rings of 10 as estimated by the $\Sigma\sigma$ is near the middle of the optimum range. The quaternary ammonium groups should provide adequate solubility and are not expected to have an adverse effect on the chemiluminescent reaction in view of the success of the quaternary ammonium oxalate ester SAPO which gave emission in an all aqueous system.

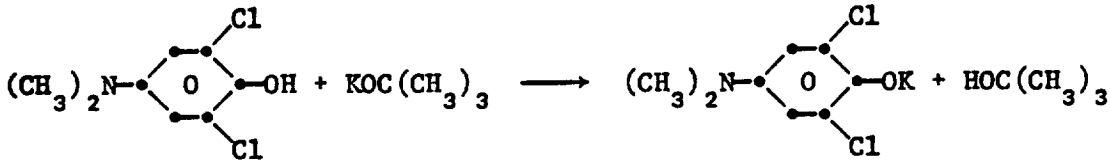
Synthesis of 10 required the intermediate 4-dimethylamino-2,6-dichlorophenol (12) which was prepared by the reductive methylation of the available primary amine (11) with formaldehyde and sodium cyanoborohydride according to the method of Borch and Hassid[9]. Although



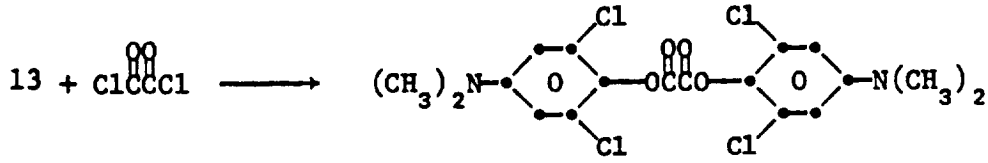
11 12 mp 78-9°

the original procedure reported yields up to 92% with a variety of tertiary amines, the best yield was 50% after several experiments under varying conditions. Infrared spectra of the by-products suggested an organo-boron compound was being formed along with 12. However, the desired tertiary amine was readily isolated from the crude product mixture and purified easily by recrystallization from hexane.

Two attempts to prepare the oxalate ester of 12 via the potassium salt 13 of the phenol were unsuccessful. In the second



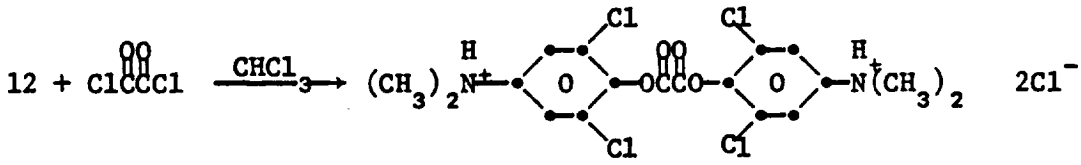
12 13



14

attempt the oxalate ester 14 was not isolated but treated with methyl trifluoromethane sulfonate immediately. The infrared spectrum of this product, however, did not indicate the presence of the expected carbonyl group.

Treatment of 12 with oxalyl chloride in chloroform gave a yellow solid believed to be the hydrochloride salt 15.

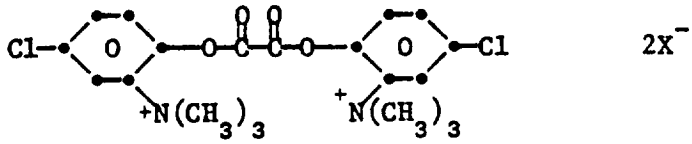


15

However, 15 was difficult to purify with very poor recovery from acetonitrile, the only recrystallization solvent which showed any promise. Qualitative chemiluminescent tests on crude 15 failed to give any detectable emission. A purple-red color indicating oxidation of the phenol was apparent immediately after mixing hydrogen peroxide with an aqueous solution of crude 15 and disodium 9,10-diphenyl-anthracene-2,6-disulfonate. Treatment of 4-dimethylamino-2,6-dichloro-phenol, 12, with oxalyl chloride in the presence of excess triethylamine afforded bis(2-dimethylamino-2,6-dichlorophenyl)oxalate (14) in 63% yield. Quaternization of this oxalate ester presented some unexpected problems. For example, treatment of 14 with a powerful alkylating agent, methyl triflate ($CH_3OSO_2CF_3$), gave a crystalline salt which when added to water regenerated 14.[2] This apparently anomalous behavior was subsequently explained by nmr which indicated the ratio of aromatic to methyl protons was close to 1:3, not the expected 1:4.5 of the desired quaternary. Elemental analysis suggested that the compound was the bistriflic acid salt of 14. The amino groups in 14 are extremely weak bases so that in aqueous solution the salt hydrolyzes to regenerate the amine 14. The quaternization of 14 was attempted several times under rigorously anhydrous conditions, but none of the desired quaternary could be isolated. Treatment of 14 with methyl iodide gave no reaction. The difficulty in quaternizing 14 is undoubtedly due to the presence of three strongly electron-attracting substituents on each of the aromatic rings causing a substantial decrease in the nucleophilic power of the tertiary amino groups. An alternate route to the synthesis of 10 was explored, quaternization of 2,6-dichloro-4-dimethylaminophenol (12) followed by treatment of the quaternary

ammonium compound with oxalyl chloride to yield the bis HCl salt 15. The quaternization reaction was carried out in an autoclave pressurized with methyl chloride gas, giving a good yield of a crystalline solid, highly soluble in water whose nmr spectrum was consistent with the structure 3,5-dichloro-4-hydroxyphenyltrimethylammonium chloride. Attempts to convert this compound to the oxalate ester were unsuccessful, however, due to insolubility of the quaternary ammonium salt in polar organic solvents.

Experimental evidence with SAPO and PAPO indicated that a somewhat less reactive oxalate may be required for optimum performance in aqueous media. Therefore, the synthesis of oxalate ester 16 was undertaken since its reactivity would be expected to be near the lower end of the optimum range ($\Sigma\sigma = 1.50$). The synthetic route

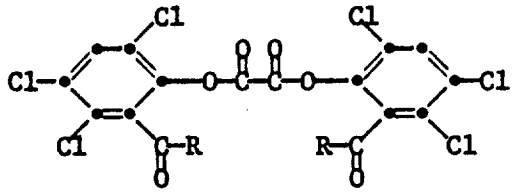



16

employed was similar to that employed for the dichlorophenyl derivative 15, reductive methylation of 2-amino-4-chlorophenol with formaldehyde and sodium cyanoborohydride to yield 2-dimethylamino-4-chlorphenol followed by oxalylation with oxalyl chloride. Treatment of the bis-hydrochloride salt with aqueous sodium bicarbonate afforded the bistertiaryamine which was quaternized with dimethyl sulfate. However, elemental analysis of the bis-quaternary ammonium salt was unsatisfactory and the crude material produced a short-lived emission in aqueous media.

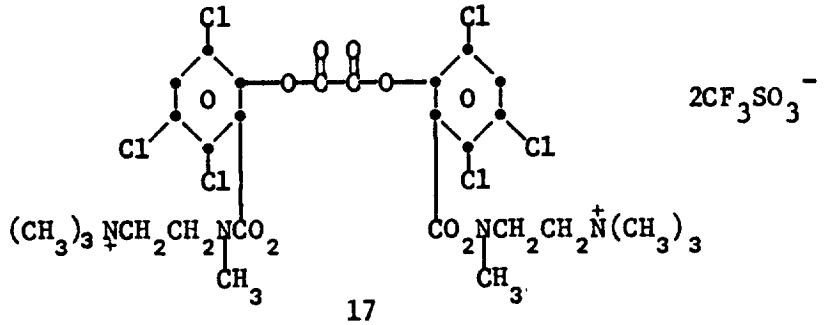
## 3. Carboxy Derivatives of Chlorophenyl Oxalates

The oxalate ester CPPO is currently employed in the nonaqueous chemical light system used in the CYALUME® lightstick. This compound has the highest light capacity of any oxalate ester prepared to date. It was designed for optimum solubility in dibutyl phthalate. The pentyl group of the ester contributes substantially to this solubility.



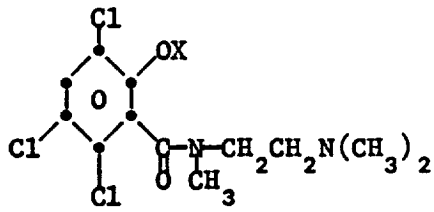
CPPO: R = $OC_5H_{11}$ ($\Sigma\sigma$ = 2.02)

This compound is highly efficient in dibutyl phthalate, but has no significant solubility in water. Introduction of a side chain containing a quaternary ammonium group instead of the pentoxy function should confer the degree of solubility needed while maintaining the efficiency of the balance of the structure. The initial step of the synthetic scheme leading to the desired oxalate ester 17 was the

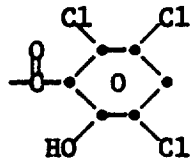


17

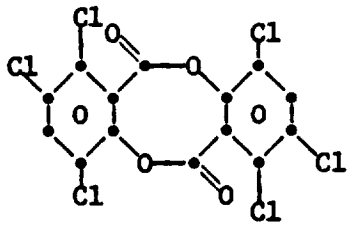
reaction of 3,5,6-trichlorosalicylic acid with thionyl chloride in an attempt to obtain the desired acid chloride. The product of the thionyl chloride reaction was treated with N,N,N'-trimethylethylene diamine and afforded a product thought to be the amide 18. Elemental analysis



18 X = H

19 X = 

suggested the product was a trichlorosalicylic acid salt of the amide 18 but mass spectrometry indicated it was a mixture of 18 and 19 along with the known[10] lactide 20. Additional attempts to prepare the acid

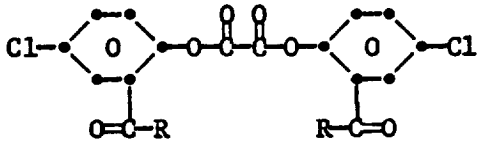


20

chloride of trichlorosalicylic failed to yield the desired material in sufficient purity for unequivocal structure assignment.

Attempts to prepare 18 by the aminolysis of pentyl 3,5,6-trichlorosalicylate also failed to yield the desired amide. Further synthetic work in the trichlorosalicylic acid series has been deferred because of the complexity and time-consuming nature of the syntheses and because of more promising leads in other areas.

On the basis of concurrent results with other oxalate esters, the optimum reactivity in aqueous solution appeared to be somewhat less than the reactivity of CPPO. Therefore, the syntheses of potentially less reactive derivatives were undertaken.



21a R = OH

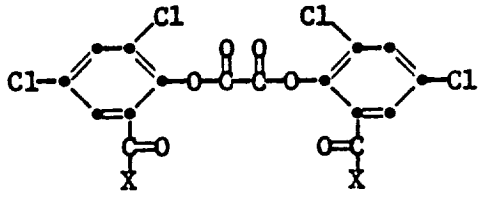
b R = Cl

c R = $OCH_2CH_2\overset{+}{N}(CH_3)_3\ Cl^-$

d R = $N(CH_3)CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$

The key synthetic intermediate, 21a, was prepared by treatment of 5-chlorosalicylic acid with an equivalent of oxalyl chloride in dry tetrahydrofuran in the presence of triethylamine. Purification of 21a proved difficult so it was converted to the bis acid chloride 21b by treatment with excess oxalyl chloride in benzene.

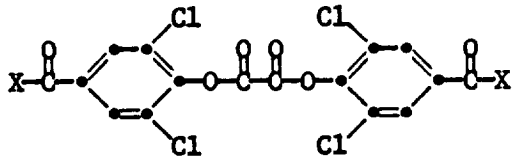
Derivatives of the isomeric oxalate esters 22a and 23a were



22a X = OH (DICO)

b X = $\underset{CH_3}{\overset{|}{N}}-CH_2CH_2\overset{\oplus}{\overset{H}{N}}(CH_3)_2\ Cl^{\ominus}$ ($\Sigma\sigma$ = 1.77)

c X = Cl



23a X = OH (CADO)

b X = $\underset{CH_3}{\overset{|}{N}}-CH_2CH_2\overset{\oplus}{\overset{H}{N}}(CH_3)_2\ Cl^{\ominus}$ ($\Sigma\sigma$ = 1.72)

c X = Cl

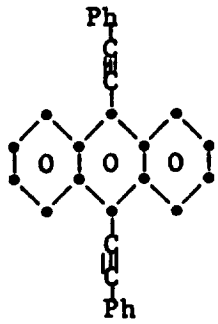
selected as candidates for synthesis since their reactivity was expected to be slightly lower than the reactive CPPO[11]. Compound CADO (23a) had been prepared in previous Cyanamid research[11], but the procedure proved to be difficult to reproduce. Subsequently, it was found that treatment of 3,5-dichloro-6-carboxybenzoic acid with oxalyl chloride in dry tetrahydrofuran affords CADO in quantitative yield. This method was also applied successfully to the preparation of DICO (41% yield). Both DICO and CADO were converted to the corresponding bis acid chlorides 22c and 23c by treatment with excess oxalyl chloride in benzene.

The acid chlorides were now available for conversion into a variety of water-soluble derivatives such as 22b and 23b. Compound 22b was prepared by treatment of the bis acid chloride 22c with N,N,N'-trimethylethylene diamine. The resultant bis-amide gave a bright, short-lived chemiluminescent emission in water.

## III. WATER-SOLUBLE FLUORESCERS

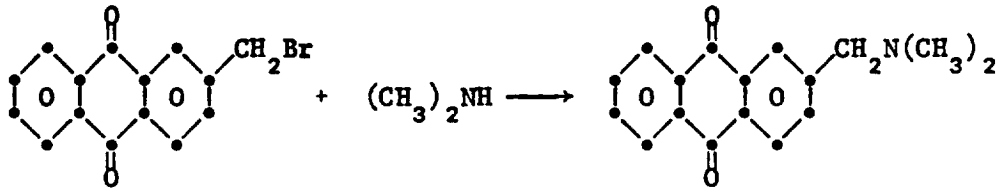
### A. Design and Synthesis

Efficient oxalate ester chemiluminescence requires a fluorescer which has a high fluorescence quantum yield, ie, high efficiency in the emission step. In addition, the fluorescer should emit radiation in the visible region of the spectrum, preferably in the green to orange spectral region where the human eye is most sensitive. The fluorescer must also be capable of efficient complex formation with the key chemiluminescent intermediate to permit efficient trapping of the energy released from the decomposition of the intermediate. Polycyclic aromatic hydrocarbons such as 9,10-bis(phenylethynyl)anthracene. (BPEA) and its chloro-derivatives have been previously employed successfully in nonaqueous chemical light systems[4a-e].




9,10-Bis(phenylethynyl)anthracene (BPEA)

Thus, one approach to a water-soluble fluorescer is to modify the structure of BPEA to introduce water solubility via the addition of substituents such as sulfonic acid salts, polyoxyethylene chains and quaternary ammonium salts to the basic BPEA nucleus. The acetylenic group is particularly labile to hydrolytic attack in strongly acid media, so the general approach used was to modify the BPEA precursor, the anthraquinone, and convert it to the corresponding BPEA derivative. This approach is illustrated below for the synthesis of the quaternary ammonium derivative (27a). The yield of 27a was 13% based on the diol 25. The elemental analysis was low for carbon but within the desired limits for hydrogen and nitrogen (mp 242-258°). Purification proved very difficult. The preparation of all phenylethynyl derivatives was carried out by modifications of the method of Reid[12].

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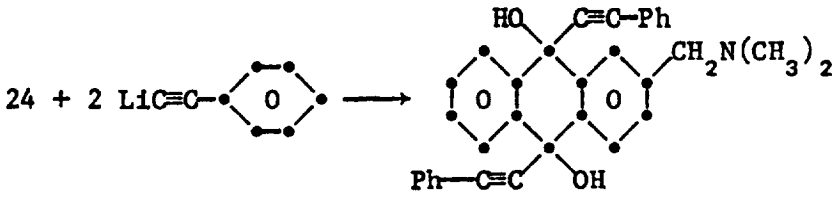


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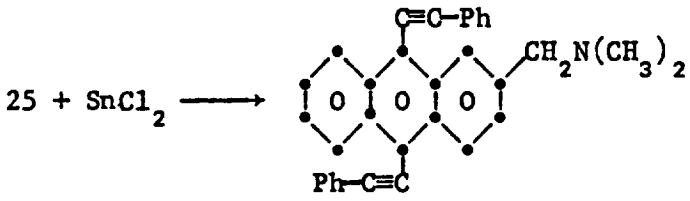


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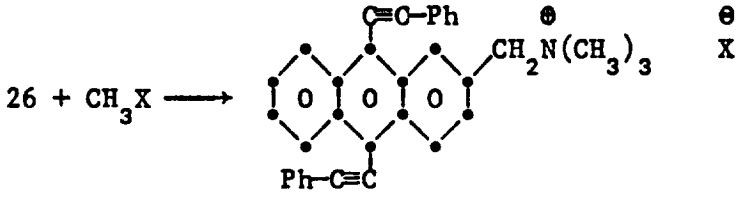
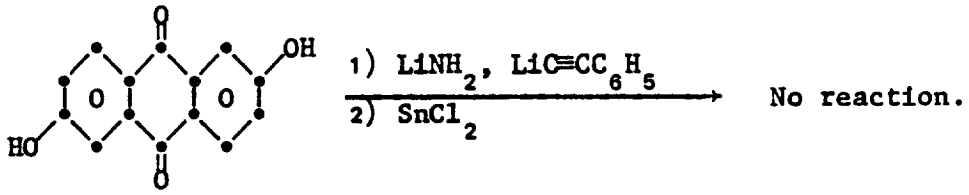


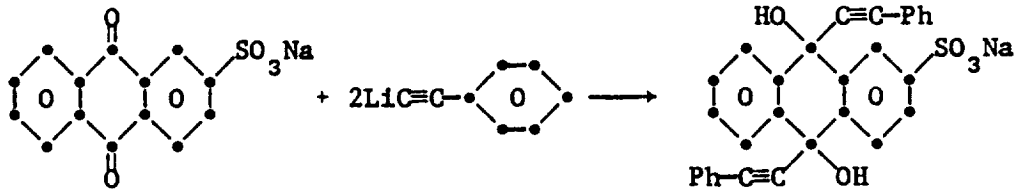

27 a. X = $SO_3CF_3$, b. $SO_3$–C$_6$H$_4$–$CH_3$, c. $OSO_3CH_3$

Attempts to carry out the addition of lithium phenylacetylide and subsequent reduction to the dilithio salt of 2,6-dihydroxyanthraquinone (28) failed to yield the corresponding 2,6-dihydroxy BPEA giving only unreacted starting material. The 2,6-dihydroxy derivative of BPEA was sought as an intermediate for polyoxyethylene and other water soluble ether-linked derivatives. Further reactions of 28 were deferred in lieu of more promising syntheses.

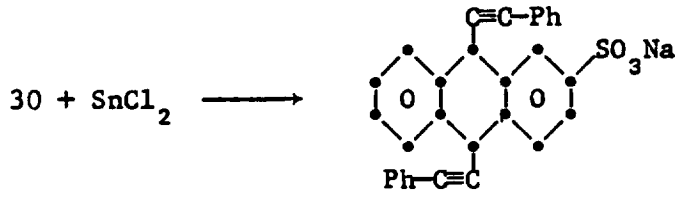



28

Attempts to prepare the 2-sulfo derivative of BPEA (31) by the scheme outlined below were also unsuccessful.

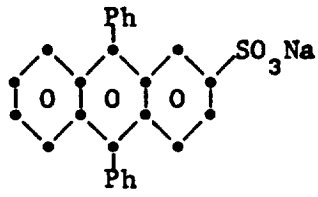



29 30




31

A second approach taken to obtain sufficient amount of fluorescer for evaluation purposes was to search the chemical reference file of the American Cyanamid Company by computer for water soluble derivatives of polycyclic hydrocarbons containing at least three fused rings which did not contain any acidic or basic functional groups. Two compounds, 9,10-diphenylanthracene-1-sulfonic acid, sodium salt (32) and pyrene-1-sulfonic acid, sodium salt (33), were found in the Cyanamid chemical reference file. Fluorescence spectra and quantum yields were measured on aqueous solutions of 32 and 33. The spectral data are summarized in the next section.

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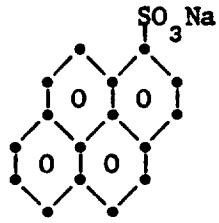
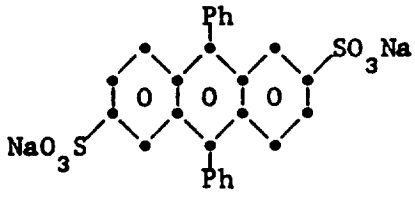


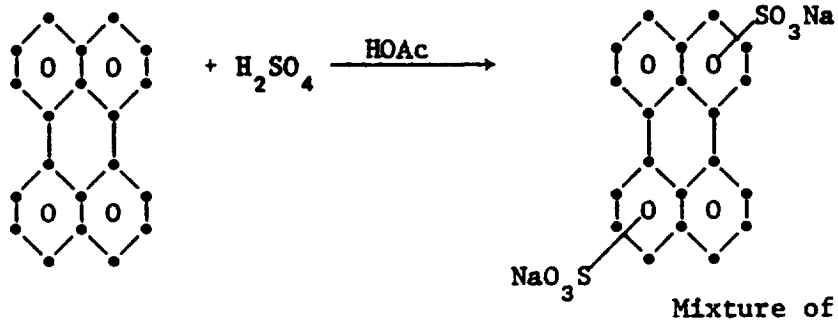

33

The anionic fluorescer 32 had a fluorescence quantum yield of 0.77 but its solubility ($5 \times 10^{-4}$ M) was too low for optimum performance in the aqueous chemiluminescent system. In an effort to improve the solubility, the disulfonate DSDPA was prepared by sulfonation of 9,10-diphenylanthracene in acetic acid-sulfuric acid as described in the literature[13]. This reaction yielded a mixture of the 2,6- and 2,7-disulfonates which were separated by salting out the less soluble 2,6-isomer. Thin layer chromatography revealed a single spot for the pure 2,6-isomer. Elemental analysis confirmed the presence of two sulfonate groups. The performance characteristics of DSDPA are described in the following section.




DSDPA

A sample of the disodium salt of perylene disulfonic acid (34) was also obtained by the sulfonation of perylene at 75-80° in a mixture of sulfuric and acetic acids according to the procedure of Marschalk[14].

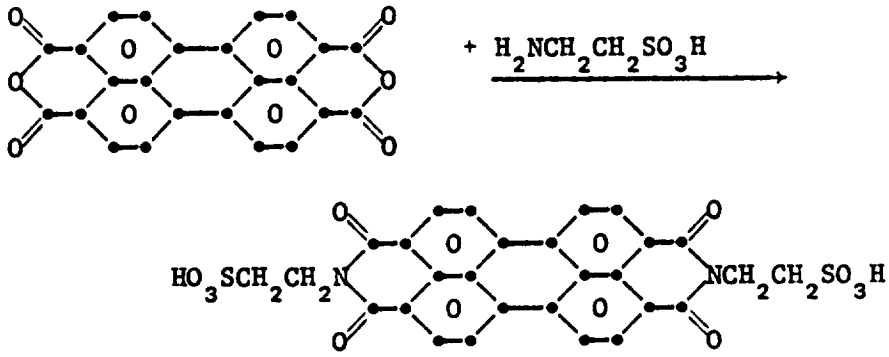



Mixture of isomers

34

The spectral data for 34 are also recorded in the following section.

Synthesis of the perylene diimide 35 was attempted by the route outlined below, because perylene and its sulfonic acid salts are known to be efficient fluorescers. It was expected that compound 35 would have adequate water solubility because of the presence of two sulfonate groups. Several attempts to condense taurine (2-aminoethanesulfonic




35

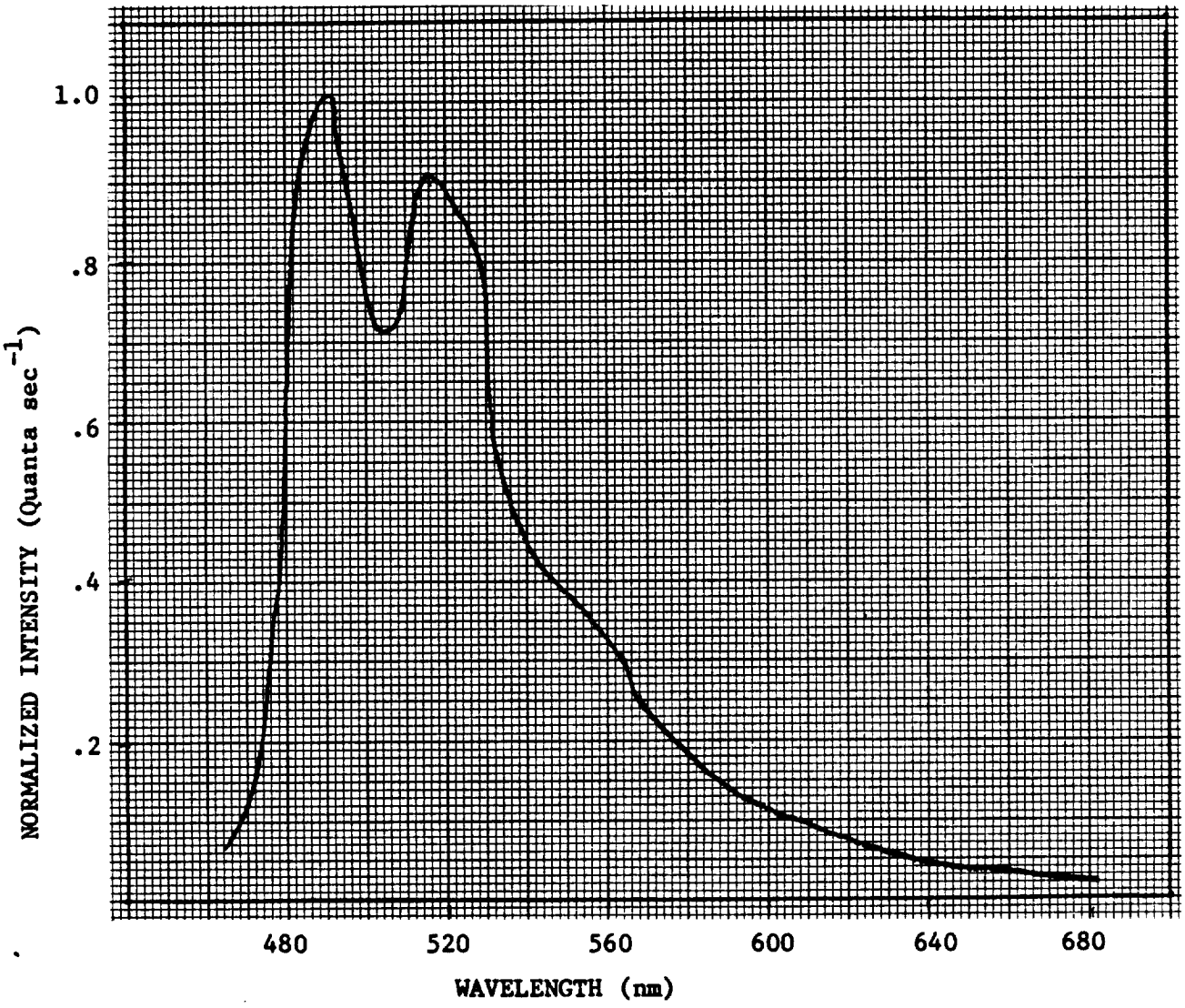
acid) with perylene dianhydride failed to yield any of the desired product 35. Large amounts of unreacted starting materials were recovered in all cases. Syntheses in this series were discontinued.

## B. Evaluation of Water-Soluble Fluorescers

The spectral properties of the fluorescers DSDPA and QBPEA are summarized in Table 2 along with those of the tetrapotassium salt of 3,4,9,10-perylene tetracarboxylic acid which was available from an independent research program. The fluorescer used in the current commercial formulation, BPEA, has been included for comparison. DSDPA had a satisfactory fluorescence efficiency with a blue emission. QBPEA had a yellow-green color similar to the emission of BPEA with a somewhat lower fluorescence efficiency. The fluorescence spectra of both QBPEA and DSDPA are illustrated in Figures 3 and 4. The spectral distribution of QBPEA in a nonaqueous chemiluminescent reaction is illustrated in Figure 5. The lower wavelength peak is no longer evident due to self-absorption in the solution. Similar effects have been observed in spectra of BPEA and its derivatives[3].

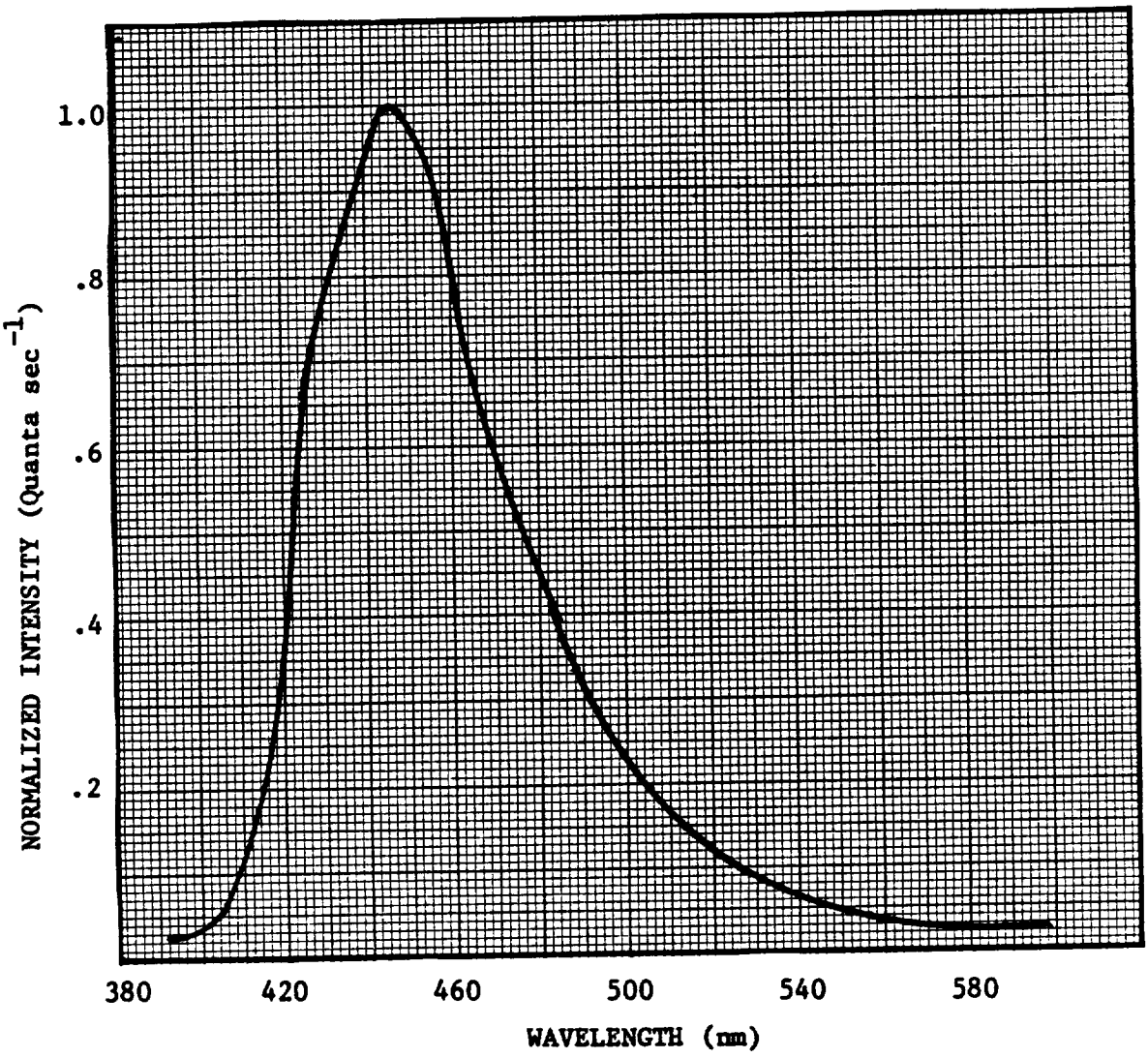
The performance of QBPEA in a nonaqueous chemiluminescent system was evaluated in order to obtain information on the effectiveness of this type of fluorescer in capturing excitation energy from the key chemiluminescent intermediate. Such information will be useful in the design of efficient fluorescers for aqueous reactions. Table 3 summarizes a comparison of BPEA and QBPEA in the CPPO chemiluminescent

Figure 3. Fluorescence spectrum of QBPEA[a]



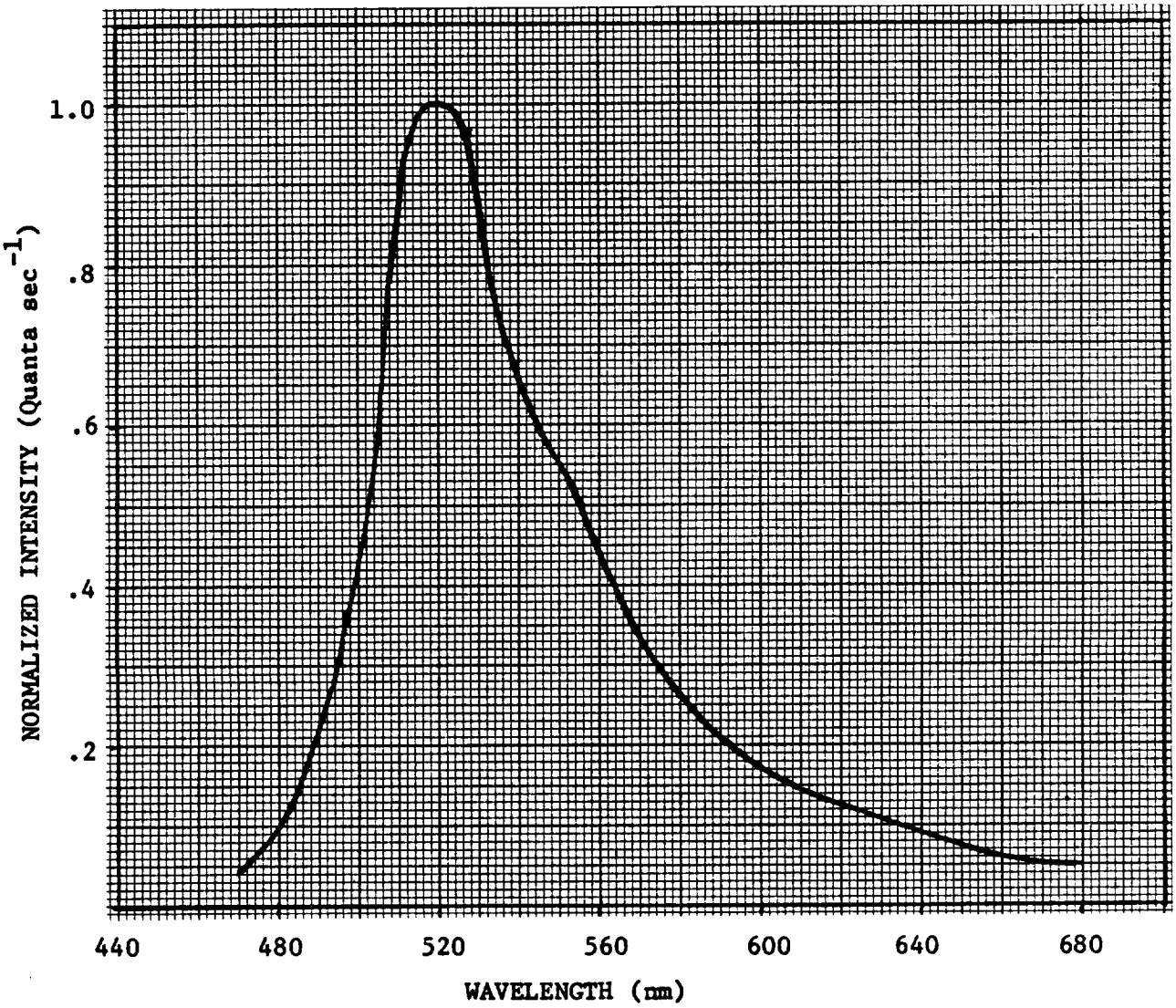

[a]Solution contained 2 x $10^{-3}$ M ([9,10-bis(phenylethynyl)-2-anthryl]methyl) trimethylammonium trifluoromethane sulfonate (QBPEA) in dibutyl phthalate. Excitation wavelength was 429 nm.

Figure 4. Fluorescence spectrum of DSDPA[a]




[a]Concentration of disodium 9,10-diphenyl anthracene-2,6-disulfonate (DSDPA) was 3 x $10^{-3}$ M in distilled water. Excitation wavelength was 362 nm.

Figure 5. Chemiluminescent spectral distribution of QBPEA[a]




[a]Chemiluminescent reaction contained 0.10 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.375 M $H_2O_2$, $1.55 \times 10^{-4}$ M sodium salicylate, and $1.13 \times 10^{-3}$ M ([9,10-bis(phenylethynyl)-2-anthryl]-methyl) trimethylammonium trifluoromethane sulfonate (QBPEA) in 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

reaction in dibutyl phthalate. Although the quantum yield obtained with QBPEA is slightly lower than with BPEA, the excitation yield[4a] (chemiluminescence quantum yield/fluorescence quantum yield) is higher, 13% for BPEA and 15% for QBPEA. Thus, QBPEA is more efficient in accepting the energy of the key chemiluminescent intermediate. The presence of the $-CH_2\overset{+}{N}(CH_3)_3$ group, a moderate electron-attracting substituent, appears to enhance the ability of the fluorescer to capture the excitation energy from the dioxetanedione. This effect could be due to a more facile donor-acceptor complex formation between the electron-rich dioxetanedione donor and the electron deficient fluorescer as the acceptor.

Table 2. Comparison of fluorescence maxima and quantum yields of BPEA and new fluorescers[a]

| Compound[b] | Solvent | Concentration | Emission Maximum | Quantum Yield |
|---|---|---|---|---|
| BPEA | Dibutyl Phthalate | 0.003M | 510 | 0.77 |
| QBPEA | Dibutyl Phahtlate | 0.002M | 520 | 0.56 |
| DSDPA | Water | 0.003M | 445 | 0.73 |
| Tetrapotassium 3,4,9,10-perylene tetracarboxylate | Water | 0.003M | 485 | 0.03 |

a Excitation wavelength was 429 nm except for DSDPA which was 362 nm.

b BPEA is 9,10-bis(phenylethynyl)anthracene. QBPEA is [(9,10-bis[phenylethynyl]-2-anthryl)methyl]trimethyl ammonium trifluoromethane sulfonate. DSDPA is disodium 9,10-diphenylanthracene-2,6-disulfonate.

Table 3. Comparison of performance of fluorescers in the CPPO chemiluminescent reaction[a]

| Fluorescer | Conc M x $10^3$ | QY[b] x $10^2$ | Light Capacity[c] | T[d] .75 | Brightness in Ft Lmbts $Cm^{-1}$ 2 Min | 10 | 30 | 60 | 120 | 180 | 240 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BPEA | 2.25 | 9.76 | 290 | | 20.5 | 16.0 | 12.6 | 7.9 | 4.3 | 2.5 | |
| QBPEA[e] | 1.5 | 8.37 | 240 | 129.7 | 43.8 | 20.4 | 10.0 | 6.2 | 3.4 | 2.5 | 2.0 |
| QBPEA[e] | 1.5 | 6.78 | 194 | 94.1 | 43.5 | 19.7 | 9.7 | 4.4 | 2.0 | 1.1 | 0.7 |

a Chemiluminescent reactions contained 0.1 M CPPO [bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate], 0.375 M $H_2O_2$, $1.55 \times 10^{-4}$ M sodium salicylate and the indicated concentrations of 9,10-bis(phenylethynyl)anthracene (BPEA) or [(9,10-bis[phenylethynyl]-2-anthryl)-methyl]trimethylammonium trifluoromethane sulfonate (QBPEA) in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol.

b Chemiluminescence quantum yield in Einstein $mole^{-1}$.

c Light capacity in lumen hours $liter^{-1}$.

d Time required for emission of 75% of the total amount of light.

e Duplicate experiments.

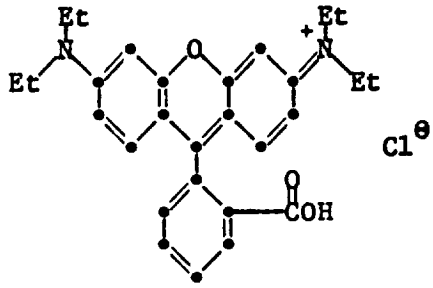
Table 4. Comparison of fluorescence spectral maxima and efficiency of polycyclic hydrocarbons and their sulfonated derivatives

| Compound | Conc $M \times 10^3$ | Emission Maximum | | Fluorescence Quantum Yield | |
|---|---|---|---|---|---|
| | | Water | Cyclohexane[15] | Water | Cyclohexane[15] |
| Pyrene | 4.4 | | 397 nm | | 0.32 |
| 1-Sulfopyrene[12] | 1.0 | 395 nm | | 0.20 | |
| Perylene | 0.32 | | 467 nm | | 0.94 |
| Disulfoperylene[13] | 1.0 | 480 nm | | 0.43 | |
| 9,10-Diphenylanthracene | 0.97 | | 428 nm | | 1.00 |
| 2-Sulfo-9,10-diphenylanthracene[11] | 0.50 | 440 nm | | 0.77 | |
| 2,6-Disulfo-9,10-diphenylanthracene | 3.0 | 435 nm | | 0.73 | |

The fluorescence spectral properties of several polycyclic aromatic hydrocarbons and their sulfonated derivatives are summarized in Table 4. In these compounds sulfonation appears to reduce the fluorescence efficiency somewhat but only small shifts in emission maxima were evident. Qualitative evaluation of the sulfonic acid salts in aqueous solution gave detectable light emission but precipitates formed with the oxalate ester SAPO. The precipitates resulted because the large organic ions of these salts have opposite charges. A quaternary ammonium substituted fluorescer would be more compatible with an ammonium substituted oxalate such as SAPO.

A series of four high purity, laser grade fluorescent dyes were obtained from Eastman Organic Chemicals for screening in an aqueous chemiluminescent formulation. The structures and spectral characteristics of these compounds are listed below.

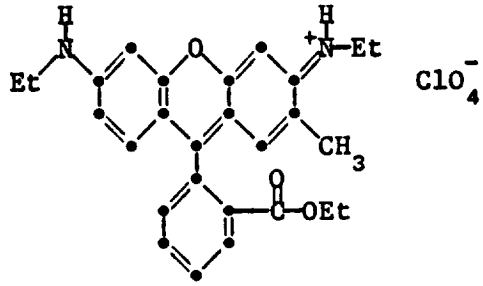
Rhodamine B (Laser Grade)



λ max abs. = 554 nm

λ max flr. = 580 nm

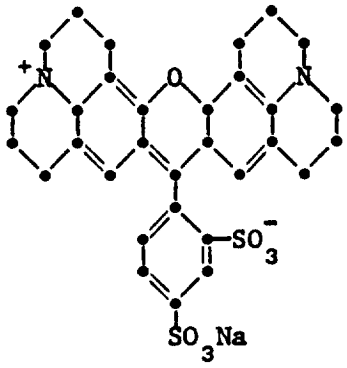
Rhodamine 6G Perchlorate



λ max abs. = 530 nm

λ max flr. = 552 nm

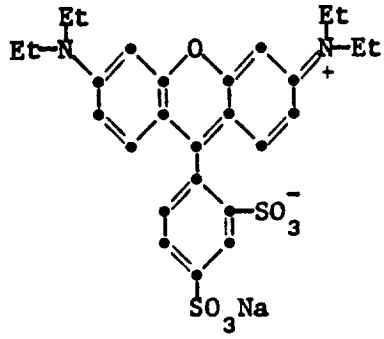
Sulforhodamine 101 (Laser Grade)



λ max abs. = 576 nm

λ max flr. = 602 nm

Sulforhodamine B (Laser Grade)



λ max abs. = 554 nm

λ max flr. = 575 nm

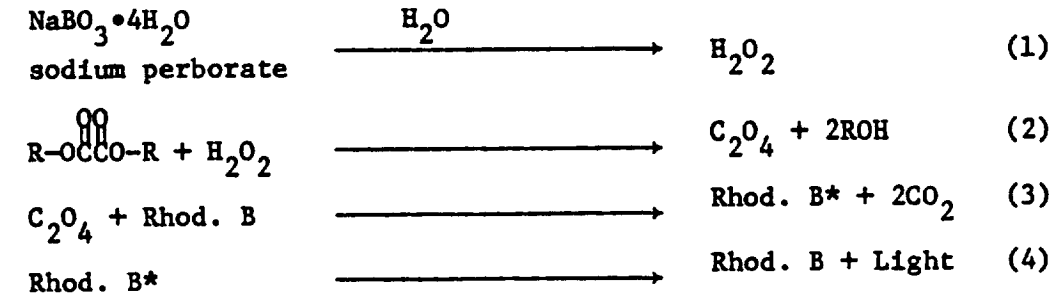
Aqueous solutions of these materials and hydrogen peroxide were prepared. The first oxalate ester active in aqueous solution, SAPO, was then added. Immediate visible chemiluminescence was observed from all four solutions. The Rhodamine B solution gave the highest intensity and emission from this solution lasted at least one hour after mixing. The Rhodamine 6G perchlorate was not very soluble in water, but did produce a very bright yellow-orange emission in the standard nonaqueous formulation with bis(2,4,5-trichloro-6-carbopentoxyphenyl)-oxalate (CPPO) and hydrogen peroxide. Addition of potassium chloride to the Rhodamine B chemiluminescent reaction had no visible effect on the light intensity and variation of the pH from 3 to 8 by use of buffers did not produce any noticeable effect. There was no visible evidence of any fluorescer decomposition.

The successful test of the rhodamines in the aqueous system is highly encouraging for several reasons: (1) the presence of chloride ion is not detrimental to the aqueous reaction, (2) the fluorescer appears sufficiently stable to the reaction, (3) the yellow-orange color of Rhodamine B should be highly visible on a road surface, (4) it is now firmly established that water does not interfere with the excitation of the fluorescer in the peroxyoxalate chemiluminescent reaction, and (5) a water-activated system can now be formulated.

## IV. FORMULATION OF WATER-ACTIVATED CHEMICAL LIGHT SYSTEM

The most effective chemiluminescent materials for aqueous reactions found thus far are the water-soluble fluorescer Rhodamine B and the water-soluble oxalate ester SAPO. These two reagents have now been combined along with sodium perborate into a free-flowing powder which generates light on contact with water. The general scheme of reactions taking place is outlined in the scheme below.

Water-Activated Chemical Light




Water reacts with sodium perborate to form hydrogen peroxide (eq. 1). The hydrogen peroxide thus liberated reacts with the oxalate ester to yield the key chemiluminescent intermediate $C_2O_4$ (eq. 2). The energy rich $C_2O_4$ then interacts with the fluorescer, Rhodamine B, to promote this fluorescer to its excited singlet state (eq. 3) which then emits light in a typical fluorescence decay process (eq. 4). This pathway is analogous to that proposed for the chemiluminescent reaction of oxalate esters in organic solvents[2] with the exception being the initiation of the process by liberation of hydrogen peroxide from sodium perborate. This represents the first example of an oxalate ester chemiluminescent reaction being <u>initiated</u> by water. The concept of producing a self-luminescent highway stripe via the action of rainfall thus appears possible.

## EXPERIMENTAL

Spectra and quantum yields for both fluorescence and chemiluminescence were obtained according to procedures previously described using the spectro-radiometer-luminometer developed by Roberts and Hirt[16]. The instrument was modified by using an RCA C31034 photomultiplier which gave satisfactory response over 350-700 nm range. The photomultiplier and monochromator were calibrated against an NBS standard tungsten lamp using the reported fluorescence quantum yield of quinine sulfate[17]. The spectra thus obtained are corrected.

Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Nmr spectra were determined on a Varian HA-100 100 MHZ instrument. Mass spectra were obtained on a Hitachi-Perkin-Elmer Model RMV-6. Melting points were determined on a "Mel-Temp" block and are uncorrected. Thin layer chromatography was carried out on Quanta QF-1 silica gel plates.

### Bis[2,4-dichloro-6-bis(2-methoxyethyl)sulfamoylphenyl]oxalate

To a solution of 10.8 g (0.081 m) of fractionally distilled bis-(2-methoxyethyl)amine and 8.68 g (12.0 ml, 0.086 m) of triethylamine in 200 ml of benzene was added with stirring a filtered solution of 20.92 g (0.08 m) of 3,5-dichloro-2-hydroxy benzenesulfonyl chloride (Aldrich Chemical Co.) in 200 ml of benzene. On the following day the slurry was washed with two 100 ml portions of 5 ml of sulfuric acid in 100 ml water, and then with a solution of 5 g of sodium bicarbonate in 100 ml of water. The benzene solution of the sulfonamide was then dried over Drierite. Removal of the solvent left a brown gum that resisted efforts at crystallization. The gum was redissolved in benzene, 11 ml of triethylamine was added and the mixture was treated with 34 ml of a 10% by volume solution of oxalyl chloride in benzene (0.04 m). After stirring overnight the mixture was filtered and the filter cake was recrystallized twice from acetonitrile (charcoal) to give 16.27 g (52% yield) of product mp 179-180°.

Calculated for $C_{26}H_{32}N_2Cl_4S_2O_{12}$:

C, 40.53; H, 4.19; N, 3.64; Cl, 18.40; S, 8.32

Found:

C, 40.49; H, 3.98; N, 3.83; Cl, 17.59; S, 8.67.

2,4,8,10-Tetrachlorodibenzo[1,5,2,6]-dioxadithiocin-6,6,12,12-tetraoxide (2)

A mixture of 5.2 g of 3,5-dichloro-2-hydroxy-benzene sulfonyl chloride and 4 ml of triethylamine in 40 ml of benzene was stirred at room temperature for three hours. The solid precipitated was collected by filtration and washed with water and ether. Yield of crude 2.2 g mp 308°. Recrystallization from chlorobenzene afforded pure 2, mp 311.5-312.5.

Calculated for $C_{12}H_4Cl_4SO_6$; mol wt 450.08

C, 32.02; H, 0.89; S, 14.25; Cl, 31.51

Found:

C, 31.97; H, 0.90; S, 14.42; Cl, 31.87.

Molecular weight by mass spectrometry was in agreement with the proposed structure.

3,5-Dichloro-2-hydroxy-N-morpholinylbenzenesulfonamide (1b)

A filtered solution of 52.2 g (0.20 m) of 3,5-dichloro-2-hydroxybenzenesulfonyl chloride in 300 ml of ether was added to a stirred solution of 34.8 g (0.40 m) of morpholine in 100 ml of ether. The product was isolated by filtration and the cake was washed with water to remove morpholine hydrochloride. One recrystallization from glacial acetic acid afforded 37.4 g (60%) of 1b, mp 147-149.

The melting point is raised to 149-150° after a second recrystallization from acetic acid.

Calculated for $C_{10}H_{11}NSO_4Cl_2$:

C, 38.47; H, 3.55; N, 4.49; S, 10.27; Cl = 22.71

Found:

C, 38.63; H, 3.49; H, 4.40; S, 10.63; Cl = 22.81.

Bis[2,4-dichloro-6-(morpholinyl)sulfamoylphenyl]oxalate

A solution of 6.1 g (0.048 m) of oxalyl chloride in 50 ml of water washed and dried chloroform was added to a mixture of 30 g (0.096 m) of 1b and 6.6 ml of triethylamine in 150 ml of chloroform. A white solid precipitated and was isolated by filtration. Recrystallization from acetonitrile followed by xylene afforded the oxalate ester,

mp 262-265°. The ir spectrum of the product revealed the characteristic oxalate carbonyl band at 1780 $cm^{-1}$.

Calculated for $C_{22}H_2N_2S_2C_{14}O_{10}$:

C, 38.95; H, 2.97; N, 4.13; S, 9.45; Cl, 20.90

Found:

C, 39.16; H, 2.99; N, 4.23; S, 10.15; Cl, 19.93.

This material is relatively insoluble in acetone, acetonitrile, benzene, xylene, chloroform, dimethylformamide, Cellosolve and water.

3,5-Dichloro-2-hydroxy-N-(2-diethylaminoethyl-N-ethylbenzenesulfonamide (1d)

A filtered solution of 23.8 g (0.09 m) of 3,5-dichloro-2-hydroxybenzenesulfonyl chloride in 75 ml of ether was slowly added to a stirred solution of 39 ml (31.4 g 0.219 mole) of N,N,N'-triethylethylenediamine (Aldrich) in 75 ml of ether cooled in an ice bath. After two hours the slurry was poured into a stirred solution of 10 g (0.119 m) of sodium bicarbonate in 200 ml of water. The mixture was then heated to evaporate the ether, cooled, filtered, and the solid washed with water (mp 152-155°C). The product was recrystallized from 300 ml of 50% ethanol, decolorizing with charcoal, yielding 23.5 g (70%) of 1d, mp 157.5-158.5°.

Calculated for $C_{14}H_{22}N_2Cl_2SO_3$:

C, 45.53; H, 6.00; N, 7.59

Found:

C, 45.46; H, 5.71; N, 7.47.

Both nmr and ir spectra were consistent with the expected structure.

Oxalylation of 3,5-dichloro-2-hydroxy-N-(2-diethylaminoethyl)-N-ethyl benzenesulfonamide (1d)

To a stirred solution of 1.85 g (0.005 m) of 1d in 50 ml of chloroform which was previously water washed and dried was added 2.5 ml of a 10% by volume solution of oxalyl chloride in dry chloroform. After twelve hours the mixture was concentrated on a rotary evaporator. Fifty ml of chloroform was added and the evaporation was repeated to remove all traces of oxalyl chloride. The resulting gum on trituration with ethyl acetate gave a crystalline solid mp 161-179, yield 1.68 g. On recrystallization from a small amount of acetonitrile a solid with mp 197-206 (erratic)

was obtained. The ir spectrum showed a single peak at 1800 $cm^{-1}$ and the product gave a chemiluminescent emission in aqueous solution when treated with hydrogen peroxide and perylene disodium sulfonate as fluorescer. Elemental analysis was not consistent with the expected structure.

Calculated for $C_{30}H_{44}N_4S_2Cl_6O_8$:

C, 41.63; H, 5.12; N, 6.47; Cl, 24.58

Found:

C, 35.05, 35.17; H, 4.33, 4.39; N, 5.25, 5.40; Cl, 26.22.

The nmr spectrum ($CD_3CN$) revealed two separate AB patterns in the aromatic region centered at 7.7 ppm and 8.03 ppm suggesting the presence of 2 sets of aromatic protons on different rings. The presence of the ethyl groups complicated the aliphatic region (3 to 4 ppm).

To a suspension of 2.17 g of the above compound in 35 ml of dry tetrahydrofuran a filtered solution of 0.6 g (0.0025 m) of potassium t-butoxide in 25 ml of tetrahydrofuran was added with stirring at room temperature followed immediately by the addition of 0.8 ml of methyl trifluoromethylsulfonate in an attempt to prepare the quaternary ammonium salt. The slurry turned translucent. After stirring overnight the filtered solution was concentrated on a rotary evaporator. An oil containing fine crystals resulted. The crystals were isolated by filtration after being slurried with ethyl acetate. A chemiluminescent emission reaction was observed when this material was treated with potassium carbonate, hydrogen peroxide and disodium perylene disulfonate in water. The light emission appeared to be largely concentrated on the surface of the undissolved solid particles of the organic compound.

The product had a double carbonyl peak at 1800 $cm^{-1}$ and a melting point of 153-156°. It was recrystallized with difficulty from a mixture of chloroform and ethyl acetate to give a solid, mp 156-168. After another recrystallization it melted at 168-171 with decomposition. The nmr spectrum of this compound was complex, but a singlet corresponding to an $R_3\overset{+}{N}CH_3$ was not clearly evident in the 3.4 to 3.5 ppm region. In addition, the 4.0 ppm region was devoid of any absorptions ascribable to the triplet of the methylene protons ($-CH_2-NR_3$).

## Sulfonation of Perylene

Perylene 2.0 g (0.008 m), was added over one hour to a stirred mixture of 12 ml of 100% sulfuric acid and 12 ml of glacial acetic acid at 73° under nitrogen according to the procedure of Marschalk[14]. After

five hours a drop of the mixture added to water gave an essentially clear yellow solution. A trace of olive-colored solid remained undissolved. The mixture was carefully poured into cold water and brought to a final volume of 175 ml and filtered to remove insolubles. Sodium sulfate (50 g) was gradually sifted into the solution to precipitate the sodium salt of the mixture of 3,9- and 3,10-perylene disulfonates. The product was isolated by filtration and washed with 10% sodium sulfate solution until a pH of 6 (Universal test paper) was noted. Final washes were made with 50% alcohol-water to remove sodium sulfate. After drying, 1.0 g (25%) of the disodium salt of the mixture of disulfonates was obtained.

{[9,10-Bis(phenylethynyl)-2-anthryl]methyl}trimethylammonium trifluoromethane sulfonate (QBPEA)

Carbon tetrachloride (3.8 l) and 190 g (0.856 mol) of 2-methylanthraquinone (Aldrich, recrystallized from acetic acid) were charged into a 12-liter flask and 800 ml of solvent distilled off to remove any moisture present. The mixture was cooled to ambient temperature, 152 g (0.854 mol) of N-bromosuccinimide (Aldrich) and 1.9 g (0.008 mol) of benzoyl peroxide were added and the slurry refluxed for 26 hours. After holding overnight at about 40°, the slurry was cooled to 5° and filtered. The solid was slurried in the flask with 1.9 liters of water on a steam bath for one hour and filtered. The small amount of solid adhering to the flask walls was rinsed out with 200 ml of acetic acid and combined with the original cake. The cake was washed with water and dried overnight in an air oven at 50°. The crude product (221 g) was found to contain several small amounts of impurities by thin layer chromatography, so it was recrystallized two times from acetic acid yielding 165 g (64%) of 2- bromomethylanthraquinone mp 198-199°, lit.[18], mp 200-201°. The ir spectrum of this product was consistent with the expected structure.

Into a three-necked, one-liter Morton flask was charged 30.1 g (0.10 mol) of the 2-bromomethylanthraquinone along with 250 ml of dimethylformamide. Dimethylamine hydrochloride (81.5 g, 1.0 mol) and 220 g (1.6 mol) of potassium carbonate hydrate were added followed by an additional 150 ml of dimethylformamide. The resulting slurry was heated while stirring to 50° and held overnight at this temperature. The reaction mixture was poured into 5 liters of distilled water and a pale yellow solid separated, was filtered and partially air-dried. The solid was dissolved in 400 ml of hot ethanol and the solution filtered to remove a small amount of insolubles. To the warm filtrate was added 15 ml of concentrated hydrochloric acid and on cooling overnight a pale yellow solid precipitated, was filtered and dried, mp 257-9° dec.,

yield 14.7 g (49%). Thin layer chromatography (methanol, silica plate) revealed a single major spot at $R_f$ = 0.55 with traces of minor components at the origin. Nmr established the structure as the hydrochloride salt of 2-dimethylaminomethylanthraquinone:

nmr (DMSO-$d_6$): δ 7.75 s, $-N(CH_3)_2$; δ 3.35, s, $\overset{+}{N}H$; δ 4.52, s, Ar-$CH_2$-N; δ 7.9-8.4, complex multiplet, 7 aromatic protons.

To 3.00 grams of the hydrochloride was added 50 ml of 5% sodium hydroxide solution and the mixture stirred for several hours. A yellow solid was filtered, washed and dried under vacuum at 65° for several hours. Yield, 1.80 g (68%) of 2-dimethylaminomethylanthraquinone. The amino compound was added to a solution of 3.06 g (0.03 mol) of phenylacetylene and 0.70 (0.03 mol) of lithium amide in 75 ml of dry dioxane which had been refluxing for 4 hours with magnetic stirring. The reaction mixture was heated to reflux. Thin layer chromatography indicated most of the starting material was consumed in 16 hours. After 40 hours of reflux, the mixture was cooled and most of the dioxane removed under reduced pressure on a rotary evaporator. A solution of 2 cc of acetic acid in 50 ml of water was added to the residue, and mixture extracted with chloroform two times. The combined chloroform extracts were washed with water and the chloroform removed on a rotary evaporatory leaving an oily residue. This residue was extracted with several portions of boiling cyclohexane, totaling 450 ml. The cyclohexane solution was treated with charcoal, filtered and concentrated to 250 ml. A brown solid precipitated from the solution on standing. The crude diol was isolated by filtration, yield 1.32 g (41%), mp 112-118 dec. Thin layer chromatography (silica gel; 4% acetic acid in methanol) indicated one major spot ($R_f$ = 0.61) and one minor spot ($R_f$ = 0.87).

The crude diol (0.46 g, 0.001 mol) was dissolved in 6 ml of dimethylformamide and 0.69 g (0.0035 mol) of stannous chloride was added and the mixture stirred overnight at room temperature. The reaction mixture was poured into water and extracted three times with chloroform, the combined extracts washed with water three times and dried over magnesium sulfate. Attempts to remove traces of blue fluorescent impurities by chromatography on silica gel were unsuccessful, so the chloroform was evaporated and the residue dissolved in 50 ml benzene and 0.02 g (0.0012 mol) of methyl trifluoromethane sulfonate was added. An orange solid precipitated within a few minutes. The mixture was stirred overnight and the solid isolated by centrifugation. The crude solid was recrystallized from acetonitrile yielding 0.08 g (13%) of the title quaternary ammonium salt, mp 242-258 dec.

Calculated for $C_{35}H_{28}NO_3SF_3$:

C, 70.10; H, 4.71; N, 2.34

Found:

C, 69.13; H, 4.96; H, 2.38.

Attempted Reaction of Perylene-3,4,9,10-tetracarboxylic Acid Dianhydride and Taurine in Sodium Acetate-Acetic Acid Mixture

A mixture of 2.5 g (0.02 mole) of taurine and 2.0 g of sodium carbonate (0.08 equiv.) and 25 ml of glacial acetic acid were heated at reflux until the evolution of carbon dioxide ceased. Perylene-3,4,9,10-tetracarboxylic acid (1.96 g, 0.005 mole) dianhydride was added and the mixture heated at reflux for three hours. The mixture was cooled to room temperature, filtered and the cake was washed with hot water. The mother liquor and washes were colorless. The red cake on the filter was shown to be unreacted dianhydride by ir spectrum.

Attempted Reaction of Potassium Perylene-3,4,9,10-tetracarboxylate and Taurine in Acetic Acid

A mixture of 1.25 g (0.01 mole) of taurine and 2.9 g (0.005 mole) of potassium perylene-3,4,9,10-tetracarboxylate in 20 ml of glacial acetic acid was heated at reflux for 5 hours. The originally orange salt produced a deep red reaction mixture. Infrared examination of the filtered, water washed product showed it to be the dianhydride. Reports in the literature indicate that the free tetracarboxylic acid has never been obtained pure because of rapid formation of the anhydride.

3,5-Dichloro-2-hydroxy-N-(2-dimethylaminoethyl)-N-methylbenzene-sulfonamide (4)

A filtered solution of 47.64 g (0.18 moles) of 3,5-dichloro-2-hydroxybenzenesulfonyl chloride in 200 ml of ether was added to a stirred solution of 55.2 ml (39.9 g 0.39 moles) of 93% N,N,N'-trimethyl-ethylenediamine in 200 ml of ether over a period of one hour and forty-five minutes. The reaction mixture was allowed to stir overnight at room temperature.

The solids were isolated by filtration, briefly washed with ether, reslurried in water and isolated by filtration, washed with a small amount of water on the filter and dried, 53.8 g (91.5% yield), mp 197-200°. The crude sulfonamide was recrystallized from 440 ml of 50% ethanol affording 46.1 g (78.5%) of pure material, mp 198-200°.

Calculated for $C_{11}H_{16}O_3N_2SCl_2$:

C, 40.37; H, 4.93; N, 8.56; S, 9.80; Cl, 21.67

Found:

C, 40.09; H, 4.78; N, 8.51; S, 9.80; Cl, 20.57, 20.71.

Disulfonation of 9,10-diphenylanthracene

To a stirred mixture of 10 g (0.003 moles) of 9,10-diphenylanthracene, 3 ml of acetic anhydride and 12 ml of acetic acid cooled in an ice bath, 12 ml of 9% fuming sulfuric acid was added over a period of forty minutes. The mixture was then heated slowly to 110 $\pm$ 5° and held at that temperature for seventy minutes. The color of the mixture turned from a light blue-green to greenish brown and finally became dark brown and fluid. After cooling to 40°, the reaction mixture was poured into a mixture of 200 ml of ice and water. The mixture was then heated to the boil and filtered through a hot filter to remove unreacted 9,10-diphenylanthracene. The filtrate was saturated with salt (70 g) at the boil and filtered.

The filter cake was washed with a little water and dried yielding 10.4 g (64%) of a disulfonate, probably largely anhydrous 2,6-isomer. It was twice recrystallized from water to give a light yellow powder, moderately soluble in water with blue fluorescence. Although the compound is reported to be a hexahydrate[6] that dehydrates at 160°, this compound appears to be largely the anhydrous salt as shown by elemental analysis.

Calculated for $C_{26}H_{28}S_2O_{12}Na_2$ (hexahydrate): C, 49.36; H, 4.46; S, 10.14

Calculated for $C_{26}H_{16}S_2O_6Na_2$ (anhydrous salt): C, 58.42; H, 3.02; S, 12.00

Found: C, 55.21; H, 3.47; S, 12.67.

Thin layer chromatography on alumina plates of the recrystallized material using a mixture of isoamyl alcohol 65 pts., acetone 50 pts., water 20 pts. and ammonia 5 pts. as eluent shows the presence of a trace of mono sulfonate in addition to the major component. No other components appear to be present.

The mother liquor from the salting out operation was neutralized and cooled but did not precipitate the other 2,7-isomer as expected. On concentration, a mixture of salts, largely sodium chloride and sodium sulfate was produced that seemed to contain some of the 2,7-isomer. Thin layer chromatography of this mother liquor showed the presence of a third component accompanied by a trace of the 2,6-isomer. The isolation of the 2,7-isomer was not pursued further since the sample of the 2,6-isomer now available would be sufficient to demonstrate the utility of an anionic fluorescer.

## Aniline Salt of 9,10-diphenyl-2,6-disulfonate

An excess of aniline hydrochloride was added to a small sample of the suspected 9,10-diphenylanthracene-2,6-disulfonate in boiling water. After two recrystallizations from 20% ethanol the tan product melted at 346-348° with blackening. The aniline salt of the 2,6-disulfonate is reported to melt at 333-334°, the 2,7-isomer salt at 305-306°.

## 9,10-Diphenylanthracene Disulfonyl Chloride

A mixture of 2 g of the crude 9,10-diphenylanthracene disulfonate sodium salt, 7 ml of phosphorous oxychloride and 5 g of phosphorous pentachloride was heated one hour at 100°. The yellow mixture was poured over ice with stirring. The solid was recrystallized from a mixture of 3 ml of acetic acid and 2 ml of benzene (considerable loss), to give a yellow solid with mp of 237°. After three recrystallizations from acetonitrile it had a fairly constant melting range of 242-263°. The melting points reported for the 2,6- and 2,7-isomers are 324-326 and 271-273, respectively. A thin layer chromatogram on a silica plate (benzene-chloroform eluent) showed the presence of a second component (blue fluorescence) surrounding the nonfluorescent yellow spot of the recrystallized sulfonyl chloride.

## 2-(3,5-Dichloro-2-hydroxy-N-methylbenzene-sulfonamido)ethyl Trimethylammonium Trifluoromethane Sulfonate Oxalate Ester (2:1) (5)

A mixture of 44.14 g (0.135 mole) of 3,5-dichloro-2-hydroxy-N-methyl-N-(2-dimethylaminoethyl)-benzenesulfonamide and 400 ml of water washed, dry chloroform was heated to boiling and 100 ml of distillate collected to insure removal of any water. The mixture was allowed to cool to 35-40° and a solution of 8.55 g (0.0795 mole) of oxalyl chloride in 60 ml of water washed, dry chloroform was added. A white solid precipitated after stirring overnight. The solid was collected by filtration, washed with a small quantity of chloroform and dried, yielding 47.45 g (89.5%) of the crude oxalate ester dihydrochloride. The ir spectrum of this material showed a single sharp band at 1775 $cm^{-1}$ indicating the presence of oxalate ester carbonyl groups. Further purification of this material proved difficult so it was carried through the next step.

To a slurry of 10.0 g (0.0128 mole) of the above oxalate ester in 150 ml of dry tetrahydrofuran was added 4.9 g (0.0297 mole) of methyl trifluoromethyl sulfonate followed immediately by 3.87 g (0.0336 mole) of potassium tert-butoxide. A mild exotherm was observed. A solid was

isolated from the reaction after stirring overnight. The crude product was recrystallized from acetonitrile, yield 6.71 g (50%), mp 210-215°. Further recrystallization from acetonitrile afforded the purified sample, mp 227-8°.

Calculated for $C_{28}H_{36}N_4O_{14}Cl_4S_4F_6$:

C, 32.22; H, 3.45; N, 5.37; Cl, 14.26; S, 12.34

Found:

C, 30.86; H, 3.55; N, 5.41; Cl, 13.48; S, 13.20.

The ir spectrum of the purified sample showed oxalate carbonyl band at 1775 $cm^{-1}$. The nmr spectrum (DMSO $D_6$) showed the following signals: δ 3.90 ppm, s, 9H, $^{+}N(CH_3)_3$; 3.97 ppm, s, 3H, $SO_2$-$\overset{+}{N}$-$CH_3$: 3.40 ppm, 3.53 ppm, 2 broad S, 4H, $SO_2NCH_2CH_2N$; 8.08 ppm; 8.35 ppm, d, 2H, Ar-H, J = 2.5 cps, meta coupling.

## Attempted Preparation of 3,5,6-Trichlorosalicyloyl Chloride

A mixture of 9.6 g (0.030 mole) of 3,5,6-trichlorosalicylic acid, 1 ml of dimethylformamide, 6.0 ml (9.9 g, 0.083 mole) of thionyl chloride and 20 ml of dry chloroform was gently warmed for two hours. The slurry gradually became a clear solution. On some occasions a solid again came out of solution. The mixture was then concentrated on a rotary evaporator, toluene was added and the concentration was repeated with gentle warming to remove all excess thionyl chloride. The residue was then taken up in toluene and used directly for amide synthesis.

For the purpose of identification the solid residue left after removal of volatiles was recrystallized from toluene giving a white solid, mp 155-157. It gave a positive test for chloride ion with silver nitrate solution.

Calculated for the acid chloride, $C_7H_2O_2Cl_4$

C, 32.35; H, 0.78; Cl, 54.56; mol wt 259.89

Found:

C, 36.69; H, 0.87; Cl = 48.01; mass spectrum; $M^{+}$ at m/e 444.

The mass spectrum suggested that this compound was the lactide 20 (lit.[10], mp 310-2°). This is not consistent with the observed mp, the presence of hydrolyzable chlorine and elemental analysis. Dimerization of the acid chloride in the inlet of the mass spectrometer could account for these apparently inconsistent results.

## Attempted Preparation of 3,5,6-Trichloro-2-hydroxy-N-(2-dimethylaminoethyl)-N-methyl Benzamide (18)

### A. From the Acid Chloride

A solution of 5 ml (3.62 g, 0.036) of 93% N,N,N'-trimethylethylenediamine in 25 ml of toluene was slowly added to a stirred solution of the "acid chloride" obtained from 9.6 g (0.030 mole) of 3,5,4-trichlorosalicylic acid prepared as described above. After one hour the solid was isolated by filtration, washed with a little toluene and dried. Crude yield 6.95 g, mp 184-188°. This compound is highly insoluble in most organic solvents but may be recrystallized from pyridine, mp 210-212°.

Elemental analysis suggested this product was the 3,5,6-trichlorosalicylic acid salt of the expected amide.

Calculated for $C_{19}H_{18}N_2Cl_6O_5$:

C, 40.24; H, 3.20; N, 4.94; Cl, 37.51

Found:

C, 42.19, 41.56; H, 3.06, 3.16; N, 5.01, 4.98; Cl, 37.20, 37.05.

Mass spectrum revealed 3 principal molecular ions at m/e 324, 444 and 546. These ions were assigned to the amide 18, the cyclic lactide 20 and the 3,5,6-trichlorosalicylic acid salt of the amide 18. Attempts to separate these components by thin layer chromatography (silica GF, pyridine eluent) were unsuccessful.

### B. From the Ester

A mixture of 8.40 ml (0.027 mole) of n-pentyl 3,5,6-trichlorosalicylate 5b and 11.6 ml (9.00 g, 0.089 mole) of N,N,N'-trimethylethylene diamine was heated at slow reflux for 24 hours. The mixture turned dark and thickened. The mixture was completely soluble in water, chloroform, ethyl acetate and nitromethane. A small amount of gummy residue remained insoluble in hexane. Saturation of a benzene solution of the product with dry hydrogen chloride yielded a gummy solid. Treatment of this solid with dilute sodium bicarbonate gave a white solid whose ir spectrum was identical with the material obtained from the acid chloride reaction in (A) above.

## Attempted Reaction of 3,4,9,10-Perylenetetracarboxylic Dianhydride and Taurine in Acetic Acid, Pyridine and Quinoline as Solvent

A mixture of 1.96 g (0.005 mole) of perylene-3,4,9,10-tetracarboxylic acid dianhydride, 2.5 g (0.02 mole) of taurine and 25 ml of glacial acetic acid were heated at reflux under nitrogen for six hours. The mixture was then cooled to room temperature and filtered. The residue on the filter was washed with hot water and dried. Both the mother liquor and wash were colorless. The infrared spectrum of the deep red residue was identical with that of the starting dianhydride.

An attempt to follow the course of the reaction with thin layer chromatography (silica plate, pyridine eluent) was unsuccessful due to the extremely low solubility of the dianhydride. It was found to be insoluble in chloroform, dimethylformamide, ethyl acetate, acetonitrile, methanol, toluene, nitromethane, carbon disulfide, acetic acid, pyridine, dimethyl sulfoxide and nitrobenzene at room temperature.

The above reaction was also tried using pyridine and quinoline as solvent, but again no reaction was observed.

## 2,6-Dichloro-4-dimethylaminophenol (12)

The procedure employed was a modification of the method of Borch and Hassid[9]. To 47.2 g (0.267 mol) of 2,6-dichloro-4-aminophenol in 250 ml of acetonitrile was added 190 ml (2.67 mol $CH_2O$) of 37% formaldehyde solution in a one liter Morton flask fitted mechanical stirrer, thermometer and condenser. A solution of 50 g (0.80 mol) of sodium cyanoborohydride (CAUTION) in 230 ml of acetonitrile was added over 2.5 hours to the above mixture which was cooled in an ice bath. The temperature during the addition was maintained at 5-10° by control of the rate of addition and the pH adjusted to near neutral with small additions of acetic acid. After completion of the addition, the ice bath was removed and the temperature was allowed to rise slowly to 60°. After a short time the temperature began to decrease, most of the solvent was then removed on a rotary evaporator under reduced pressure. The residue was extracted with two portions of diethyl ether totaling about 500 ml. The ethereal solution was extracted twice with saturated sodium bicarbonate and the ether evaporated overnight in the hood leaving a dark red oil. This oil was extracted three times with boiling hexane, the combined extracts treated with activated charcoal and concentrated to about 300 ml on the steam bath. An off-white solid came out on cooling, yield 35.2 g (64%) of 2,6-dichloro-4-dimethylaminophenol, mp 65-77°, thin layer chromatography on silica ($CHCl_3$ development) gave a single major spot at $R_f$ 0.70 with traces of impurities at $R_f$ 0.35 and

0.85. A second recrystallization afforded 27.5 g (50%) of the phenol mp 74-77.5. Tlc indicated two very minor impurities. This material was sufficiently pure for further synthesis.

The analytical sample was prepared by three additional recrystallizations from hexane, mp 78-9°, tlc one spot on silica.

Calculated for $C_8H_9NOCl_2$:

C, 46.63; H, 4.40; N, 6.80; Cl, 34.41

Found:

C, 46.78; H, 4.32; N, 6.72; Cl, 34.47.

ir (Nujol): 3100-3200, broad; 1500, 970, 865, 840 805 and 769 $cm^{-1}$.

nmr ($CDCl_3$): δ 2.83 ppm, s, 6H; δ 5.27, broad s, 1H; δ 6.63, s, 2H.

2-(Morpholinyl)methylanthraquinone

Into a one liter Morton flask fitted with stirrer and condenser was charged 40 g (0.133 mol) of 2-bromothylanthraquinone and 700 ml of dichloromethane. To this mixture while stirring was added 70 ml (0.80 mol) of morpholine rapidly in several portions. The resulting solution was stirred for 3 days at room temperature. The solvent was removed under reduced pressure on a rotary evaporator and the residue washed with 100 ml of 7% sodium hydroxide solution, filtered, washed with water and air-dried. Two recrystallizations from cyclohexane afforded 28.2 g (69%) of 2-(morpholinyl)methylanthraquinone, mp 120-121. Tlc ($CHCl_3$) revealed a single major component at $R_f$ 0.30 with faint traces of two impurities. Further recrystallization from cyclohexane afforded the pure sample mp 122-123.5°.

Calculated for $C_{19}H_{17}NO_3$:

C, 74.25; H, 5.58; N, 4.56

Found:

C, 74.21; H, 5.59; N, 4.32.

ir (Nujol): 1670, 1330, 1300, 1120 and 720 $cm^{-1}$.

A second crystalline form of this compound, mp 104-5°, was encountered in the recrystallization from cyclohexane. The ir of this material was virtually identical to that of the mp 122-123.5 form.

## Reaction of 2,6-Dichloro-4-dimethylaminophenol with Oxalyl Chloride

(a) Potassium Salt Method

To 25 ml of dry dioxane (pesticide grade stored under nitrogen and dried with magnesium sulfate immediately prior to use) was added 1.17 g (0.010 mol) of potassium tert-butoxide and 2.07 g (0.010 mol) of 2,6-dichloro-4-dimethylaminophenol. The mixture was stirred, heated to reflux and held at reflux for 0.5 hour. After allowing to cool to room temperature, 0.43 ml (0.63 g, 0.005 mol) of oxalyl chloride was added. This mixture was heated at reflux for 2 hours, cooled to room temperature overnight and filtered, washing the solid with dioxane. Evaporation of the dioxane from the filtrate give an oil which crystallized slowly. The ir of this solid was identical to 2,6-dichloro-4-dimethylaminophenol.

(b) Direct Reaction Method

To 25 ml of dry (over magnesium sulfate) chloroform was added 2.07 g (0.010 mol) of 2,6-dichloro-4-dimethylaminophenol. While stirring 0.43 ml (0.63 g, 0.005 mol) of oxalyl chloride was added rapidly resulting in a slight exotherm. A white precipitate formed immediately. The mixture was heated to reflux and held for two hours. After cooling overnight, the solvent was evaporated under reduced pressure leaving a light brown crystalline residue. The ir spectrum of this material showed amine hydrochloride at 2520 and 2450 $cm^{-1}$ and oxalate carbonyl bands at 1770 and 1720 $cm^{-1}$. This solid did not melt cleanly with decomposition beginning at about 195° and extensive decomposition with gas evolution occurring between 208 and 220°. A number of solvents for recrystallization proved to be unsatisfactory because of poor solubility including, benzene, chloroform, chlorobenzene, ethyl acetate and dioxane. Most of the residue was dissolved in 200 ml of acetonitrile. This solution was filtered to remove a small amount of undissolved material and the filtrate concentrated to 50 ml. A yellow solid crystallized on cooling of the solution. This solid was recovered by filtration and air-dried on the filter. The ir showed amine hydrochloride bands at 2500 and 2400 $cm^{-1}$, a carbonyl band at 1760 $cm^{-1}$ and two other strong absorptions at 1120 and 810 $cm^{-1}$. Elemental analysis indicated this material was impure. A qualitative chemiluminescent test on this solid in aqueous solution gave no detectable emission.

## 3,5-Dichloro-4-hydroxybenzenesulfonyl Chloride

Chlorosulfonic acid, 460 g (260 ml, 2.52 moles) was added to a solution of 100 g (0.61 mole) of 2,6-dichlorophenol in 200 ml of carbon

disulfide at 0-5° over a period of 105 minutes. Stirring was continued for one hour after the addition and the mixture allowed to warm to room temperature. The mixture was then very carefully (a violent reaction) poured into 2.5 liters of a mixture of ice water. The solid which precipitated was isolated by filtration, washed with water and dried overnight under partial vacuum under a stream of air yielding 150 g (94%) of crude sulfonyl chloride. Recrystallization from a mixture of 300 ml toluene and 300 ml heptane with charcoal decolorizing gave 127 g (80% yield) of the pure sulfonyl chloride, mp 123-4°, lit.[19], mp 125°.

3,5-Dichloro-4-hydroxy-N-methyl-N-(2-dimethylaminoethyl)-benzenesulfonamide (4)

A solution of 13.5 g (0.05 mole) of 3,5-dichloro-4-hydroxy-benzenesulfonyl chloride in 60 ml of ether was added dropwise via a syringe pump over one hour to a solution of 5.4 g (purity 93%, contains 5.1 g, 0.05 mole) of N,N,N'-trimethylethylene diamine in a mixture of 30 ml of dimethylformamide and 30 ml of acetonitrile. A cream colored solid precipitated, was isolated by filtration, washed with dilute sodium bicarbonate solution and dried. The yield of crude sulfonamide was 10.5 g (64%). Recrystallization from dimethylformamide afforded 7.8 g (48%) of the pure material, mp 242-243.

Calculated for $C_{11}H_{16}N_2SCl_2O_3$:

C, 40.37; H, 4.93; N, 8.56; Cl, 21.67; S, 9.80

Found:

C, 40.08; H, 4.78; N, 8.48; Cl, 21.21; S, 9.55.

Bis-{2,6-dichloro-4-[(2-dimethylaminoethyl)methylsulfamoyl]phenyl} Oxalate, Dihydrochloride (SAPO)

A suspension of 6.54 g (0.01 mole) of 3,5-dichloro-4-hydroxy-N-methyl-N-(2-dimethylaminoethyl)-benzenesulfonamide in 60 ml of dry pyridine was treated with 22 ml of a toluene solution containing 1.2 g (0.005 mole) of oxalyl chloride. A gelatinous precipitate separated and was filtered. Filtration was quite slow, yielding 6.09 g (78%) of crude product (mp started 240-245, dec. 257). The infrared spectrum of the off-white solid indicated the presence of the typical oxalate carbonyl band and an amine hydrochloride band. This material is being purified for analysis. Treatment of the crude oxalate hydrochloride with dilute aqueous sodium bicarbonate regenerated the starting sulfonamide presumably by hydrolysis of the oxalate ester.

Addition of a sample of the crude oxalate hydrochloride to an aqueous solution of Rhodamine B and dilute hydrogen peroxide gave a very bright chemiluminescent emission which lasted several seconds. Variation of the pH of the medium from 3 to 8 had no visible effect on the light output. Mixing of the crude oxalate hydrochloride and Rhodamine B followed by hydrogen peroxide gave no light. However, addition of solid oxalate to this solution immediately generated bright emission. This suggests that the oxalate ester is decomposing in water at a reasonably rapid rate.

## Bis-(2,6-Dichloro-4-dimethylaminophenyl)-oxalate (14)

A solution of 10.3 g (0.05 moles) of 2,6-dichloro-4-dimethylaminophenol in 200 ml of benzene was heated to remove 50 ml of distillate (azeotropic distillation). Fifty ml of triethylamine (36.5 g, 0.36 moles) was then added followed by the slow addition of 2.14 ml (3.18 g, 0.025 moles) of oxalyl chloride in 20 ml of benzene. A yellow solid separated (12.1 g) which was isolated by filtration and washed with a little benzene. The compound is remarkably insoluble in most common solvents. Although it may be recrystallized from dimethylformamide, decomposition often occurs. Recrystallization from nitrobenzene afforded a bright yellow solid 7.3 g (63%), mp 287-88. Ir: strong carbonyl at 1750. The mass spectrum was in agreement with the expected structure.

Calculated for $C_{18}H_{16}N_2Cl_4O_4$:

C, 46.36; H, 3.46; N, 6.01; Cl, 30.42

Found:

C, 46.37; H, 3.50; N, 5.85; Cl, 30.35.

## Attempted Quaternization of Bis-(2,6-dichloro-4-dimethylaminophenyl) oxalate

To 1.0 g of bis-(2,6-dichloro-4-dimethylaminophenyl)oxalate in 100 ml of hot dioxane was added 2 ml of methyl trifluoromethanesulfonate. A white precipitate formed immediately, was isolated by filtration, ether washed and dried. Recrystallization of the crude material from acetonitrile afforded a white solid, mp 302-3, in poor recovery. Addition of this material to water regenerated the starting oxalate ester, confirmed by ir, nmr and mp. Nmr revealed the ratio of $N-CH_3$ to aromatic ring protons to be 6:2. Elemental analysis suggested the material was the di-trifluoromethane sulfonic acid salt of the bis-amino oxalate.

Calculated for $C_{20}H_{18}N_2Cl_4F_6S_2O_{10}$:

C, 31.34; H, 2.37; N, 3.66; Cl, 18.51; F, 14.88; S, 8.37

Found:

C, 30.96; H, 2.45; N, 3.23; Cl, 18.18; F, 18.1; S, 8.53.

Attempts to quaternize the amino oxalate ester with methyl iodide and dimethyl sulfate were unsuccessful.

## Bis(4-carboxy-2,6-dichlorophenyl) Oxalate (23a, CADO)

Into a 500-ml round-bottom flask fitted with stirrer, condenser, thermometer and drying tube was charged 200 ml of dry tetrahydrofuran followed by 30.6 g (0.15 mol) of 3,5-dichloro-4-hydroxybenzoic acid and 21 ml (0.15 mol) of triethylamine. The flask was cooled in an ice bath and 6.4 ml (0.075 mol) of oxalyl chloride was added with stirring dropwise over 40 minutes. The ice bath was removed and the mixture allowed to warm to room temperature over two hours. A white solid (20.3 g), triethylamine hydrochloride, was filtered and washed with dry tetrahydrofuran and the filtrate evaporated to yield 35.2 g (quantitative yield) of CADO, mp 258-262 (sealed tube, dec), lit. mp 250-252 (dec). The infrared spectrum was consistent with the expected structure, with two characteristic carbonyl absorptions evident at 1820 and 1710 $cm^{-1}$. The low solubility of this oxalate ester in most organic solvents precluded preparation of an analytically pure sample so the CADO was converted to the acid chloride 23c for purification and characterization.

## Bis(4-chlorocarbonyl-2,6-dichlorophenyl) Oxalate (23c)

Benzene (75 ml) was charged into a 250-ml round-bottom flask fitted with magnetic stirrer and azeotroped to dry. After cooling to about 50°, 4.67 g (0.01 mole) of CADO was added followed by 4.3 ml (0.05 mol) of oxalyl chloride. Foaming was evident at this point. After heating 30 minutes at reflux, all the solid dissolved and the foaming subsided. The mixture was held 90 additional minutes at reflux and allowed to cool overnight. The benzene was removed on a rotary evaporator under vacuum. Benzene (50 ml) was added, evaporated to remove excess oxalyl chloride and the process repeated. The crude acid chloride was washed with hexane leaving a crystalline solid, 1.81 g (36%) mp 123-8 (dec with gas evolution). The infrared spectrum of this material showed the expected carbonyl absorptions at 1780 and 1740 $cm^{-1}$. The absorptions of the carboxyl group were no longer evident. Several recrystallizations from cyclohexane afforded 3b, mp 144-7°. The mass spectrum of this material confirmed the structure with the characteristic six chlorine isotope pattern at m/e 502 (M) and other characteristic

fragments at m/e 474 (M-28), 467 (M-35), 251 (base peak, M/2) and 207 (M/2-44). The elemental analysis of this material was unsatisfactory, probably due to slight hydrolysis of the sample.

Calculated for $C_{16}H_4O_6Cl_6$:

C, 38.06; H, 0.80; Cl, 42.13

Found:

C, 38.85; H, 1.15; Cl, 41.21.

## Bis(2,4-dichloro-6-carboxyphenyl) Oxalate (22a, DICO)

Into 400 ml of dry tetrahydrofuran was charged 41.4 g (0.20 mol) of 3,5-dichlorosalicylic acid and 28 ml (0.20 mol) of triethylamine. The solution was cooled to 2° in an ice bath and 8.5 ml (0.10 mol) of oxalyl chloride was added dropwise with stirring over one hour. The solid-liquid mixture was allowed to warm to room temperature, a white solid, triethylamine hydrochloride, filtered and washed twice with tetrahydrofuran. Evaporation of the solvent from the filtrate gave a white solid which was washed with benzene followed by hexane and air dried, yield 19.3 g (41%), mp 174-8 dec. The infrared spectrum of this material was consistent with the expected structure; carbonyl bands at 1800 and 1720 $cm^{-1}$; weak carboxyl bands at 2550 and 2630 $cm^{-1}$ and strong ester C-O band at 1120 $cm^{-1}$. Poor solubility of this material in most organic solvents prevented further purification so the DICO was converted to the acid chloride 22c for characterization.

## Bis(2,4-dichloro-6-chlorocarbonylphenyl) Oxalate (22c)

To 28.1 g (0.06 mol) of DICO in 150 ml of azeotropically dry benzene was added 26 ml (0.31 mol) of oxalyl chloride over 30 minutes at room temperature. Some foaming was evident. The mixture was refluxed for one hour at which point solution was complete. The solvent was removed on a rotary evaporator and an additional 100 ml of benzene added and removed under reduced pressure. The residue was recrystallized twice from toluene, yield 16.5 g (55%) mp 164-165. Additional recrystallizations from toluene resulted in no mp change.

Calculated for $C_{16}H_4O_6Cl_6$:

C, 38.06; H, 0.80; Cl, 42.13

Found:

C, 38.33; H, 1.26; Cl, 42.85.

## Attempted Preparation of 2-Hydroxy-5-chlorobenzene Sulfonyl Chloride

Into a 2-liter round-bottom flask was charged 128.6 g (1.0 mol) of p-chlorophenol and 643 ml of chloroform. The solution was cooled to 0° and while stirring 233 g (2.0 mol) of chlorosulfonic acid was added dropwise while maintaining temperature at 0° or below with an ice-methanol bath. The reaction mixture was allowed to warm to room temperature overnight after which two layers separated. The top (chloroform) layer amounted to 838 g while the bottom layer weighed 322 g. Quenching of each layer separately into ice failed to yield any of the desired sulfonyl chloride. Addition of a sulfuric acid solution of p-toluidine to the quenched acid layer gave 81.1 g of the p-toluidine salt of 2-hydroxy-4-chlorobenzenesulfonic acid (26%), mp 181.5-187.0. Recrystallization of this salt from isopropanol afforded the analytically pure sample, mp 228-231.

Calculated for $C_{13}H_{14}O_4NSCl$:

C, 49.45; H, 4.47; N, 4.34; S, 10.15; Cl, 11.23

Found:

C, 49.66; H, 4.66; N, 4.34; S, 10.04; Cl, 11.38.

This establishes that the major product from the chlorosulfonation reaction is the sulfonic acid. A number of experimental variations on the above method were attempted and literature reports to the contrary none of the desired sulfonic acid was obtained. Treatment of the sodium salt of 2-hydroxy-5-chlorobenzenesulfonic acid with phosphorus pentachloride in phosphorus oxychloride gave none of the expected sulfonyl chloride, literature[20] mp 114°.

## Quaternization of 4-Hydroxy-3,5-dichloro-N,N-dimethylaniline

Into a 300-ml stirred autoclave was charged 15.0 g (0.073 mol) of 4-hydroxy-3,5-dichloro-N,N-dimethylaniline and 60 ml of anhydrous methanol. The autocalve was pressurized to 60 psig with methyl chloride and heated 2.5 hours at 100° (max pressure 185 psig). The autoclave was allowed to cool overnight and its contents discharged. The methanol was evaporated and the residue extracted with benzene to remove unreacted tertiary amine, leaving a grey tan solid. This solid was readily soluble in water, giving a positive silver nitrate test. It was recrystallized from isopropanol but tended to produce a yellow coloration when its solutions were exposed to air. The nmr spectrum of this material was consistent with the expected structure. However, attempted oxalylation with oxalyl chloride in acetonitrile or tetrahydrofuran was unsuccessful, probably due to the low solubility of the salt in these solvents.

## Bis(2-carboxy-4-chlorophenyl)oxalate (BCCO)

Triethylamine (29 ml) was added to a stirring solution of 34.5 g (0.2 mol) 5-chlorosalicylic acid dissolved in 250 ml of dry tetrahydrofuran (THF). IMPORTANT! The THF must be carefully dried, typically over molecular sieves, to reproduce the yield and purity. The solution was cooled in an ice bath while protecting from moisture and 8.4 ml of oxalyl chloride added dropwise over one hour. Triethylamine hydrochloride precipitated from the solution immediately on addition of the oxalyl chloride. The mixture was stirred for 2 hours after completion of the addition and the amine hydrochloride removed by filtration. The triethylamine hydrochloride was slurried with hot THF and filtered again to ensure complete removal of the product. Evaporation of the THF on a rotary evaporator afforded 44.2 g of a pasty cream-colored solid. Washing this solid with benzene yielded 17.1 g (43%) of BCCO, mp 150-151° (dec. with gas evolution). The infrared spectrum of this material was consistent with the expected structure, showing both the oxalate and carboxy carbonyl groups at the expected wavelengths. Attempts to purify the material further by recrystallization from a variety of solvents were unsuccessful due to decomposition of the material. It was, therefore, used without further purification in the following reactions.

## Attempts to Prepare Ester and Amide Derivatives of BCCO

Preparation of the bis acid chloride of BCCO was carried out according to the same general procedure used for the corresponding dichlorophenyl derivative. To 20 g (0.05 mol) of BCCO slurried in 250 ml of dry benzene was added 47.7 ml (0.56 mol) of oxalyl chloride dropwise, rapidly using a magnetic stirrer for agitation. After all the oxalyl chloride had been added, some of the BCCO remained insoluble. Heat was applied to the flask gently via a "heat gun" blower, appreciable foaming and gas evolution were apparent as the heating continued and were controlled by the rate of heating. After the gas evolution ceased, the clear solution was refluxed for one hour. After standing two days at room temperature, the benzene was removed on a rotary evaporator under vacuum. Dry benzene (250 ml) was added and evaporated on the rotavap twice in order to ensure complete removal of excess oxalyl chloride. Infrared spectrum on the oily residue indicated all of the carboxyl groups had reacted and a single broad band at 1780 $cm^{-1}$ was indicative of both the oxalate carbonyl and the acid chloride carbonyls.

This acid chloride was treated with N,N,N'-trimethylethylenediamine and choline chloride in an attempt to prepare the corresponding bis-amide and bis-ester, respectively. The crude products in both cases were very hygroscopic and formed oily mixtures very rapidly on contact with the atmosphere.

## Formulation of Water-Activated Chemiluminescent System

A 2.0-g sample of 2-(3,5-dichloro-2-hydroxy-N- methylbenzene-sulfonamido)ethyl-N,N-dimethyl ammonium chloride oxalate (2:1) (SAPO·HCl) was added to a solution of 0.02 g of Rhodamine B (Eastman No. 14352, laser grade) in 20 ml of dry chloroform in a 50-ml round bottom flask. The solvent was then removed from the mixture under reduced pressure on a rotary evaporator leaving a purple solid. Sodium perborate (4.0 g) was added to this solid and the flask containing a magnetic stirring bar rotated for about one hour to produce a uniform mixture.

Chemiluminescent emission is produced from this mixture by addition of an equal volume of water in a test tube. Alternatively the solid can be spread on a flat surface and chemiluminescent emission initiated by spraying a fine mist of water onto the solid. The emission produced by either method lasts approximately 5 to 10 minutes depending on the amount of water used.

## 2-Dimethylamino-4-chlorophenol

To 76.66 grams (0.534 mole) of 2-amino-4-chlorophenol in 500 ml of acetonitrile was added 380 ml (5.34 mole) of 37% formaldehyde solution in a two-liter Morton flask fitted with a mechanical stirrer, thermometer and condenser. A solution of 100 grams (1.6 mole) of sodium cyanoborohydride in 460 ml of acetonitrile was added dropwise over a four-hour period to the above mixture at 5-10° by cooling in an ice bath. During this period several small additions of acetic acid were made to bring the pH near 7. After stirring for three hours the reaction mixture was slowly heated to 60°C and held for 30 minutes. The reaction mixture was then allowed to cool to room temperature. The solvent (acetonitrile) was then removed under vacuum on a rotary evaporator leaving an oily, red-brown residue which was extracted with two portions of diethyl ether totaling about one liter. The combined ethereal extracts were extracted twice with a saturated solution of sodium bicarbonate totaling one liter. The ether was then removed on the rotary evaporator leaving a dark brown solid residue. The above brown solid material was extracted four times with boiling hexane totaling 1500 ml. The hexane solution was then decanted from a black tar-like material also present, and treated with Darco G-60 activated charcoal.

The solution was filtered through Hyflo filter cel, concentrated to 250 ml on a steam bath and an off-white solid precipitated out on chilling.

The yield of crude 2-dimethylamino-4-chlorophenol was 68.94 grams (75%). Recrystallization from petroleum ether with Darco G-60 treatments afforded 55.48 grams (61%) of the pure material, mp 53-54°C.

Calculated for $C_8H_{10}ClNO$:

C, 55.98; H, 5.87; Cl, 20.66; N, 8.16

Found:

C, 56.22; H, 5.94; Cl, 19.98; N, 8.24.

Bis(2-dimethylamino-4-chlorophenyl)oxalate Dihydrochloride

To a stirring solution of 6.9 grams of dimethylamino-4-chlorophenol in 50 ml of dry tetrahydrofuran (THF) was added dropwise a solution of 2.5 grams oxalyl chloride in 25 ml dry THF. The reaction mixture was stirred for 3 hours and the resulting white precipitate was isolated by filtration, mp 180°C (yield 88%).

Calculated for $C_{18}H_{20}O_4Cl_4N_2$:

C, 45.98; H, 4.29; Cl, 30.16; N, 5.97

Found:

C, 45.85; H, 4.57; Cl, 29.06; N, 5.63.

{Oxalylbis[oxy(5-chloro-o-phenylene)]}bis(trimethylammonium Methyl Sulfate) (BTAO)

To 10.0 grams (0.021 mol) of bis(2-dimethylamino-4-chlorophenyl)-oxalate dihydrochloride was added 400 ml of 5% aqueous sodium bicarbonate and the resulting mixture stirred for one hour. The amino oxalate (9.78 g) was isolated by filtration, mp 45-55° gas evol., melt 60-65°. The crude oxalate was recrystallized from hexane, azeotroping the solution first to insure complete removal of water; the yield was 5.88 grams, mp 118° gas evol., melt 124-8°. The oxalate was then dissolved in 400 ml of benzene and the solution azeotroped to dry.

After cooling to room temperature, a solution of 4.98 ml (6.62 g, 0.05 mol) of dimethyl sulfate in 30 ml of dry benzene was added dropwise over one hour. The white precipitate which formed was filtered and washed with a small quantity of benzene. The yield of bis-quaternary ammonium compound (BTAO) was 3.27 g (24%); mp 165° gas evol., melt 168-170°.

Calculated for $C_{22}H_{30}O_{12}Cl_2N_2S_2$:

C, 40.68; H, 4.66; Cl, 10.92; N, 4.31; S, 9.87

Found:

C, 38.50; H, 4.37; Cl, 11.35; N, 4.46; S, 10.46.

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## APPENDIX I

### Chemically Luminescent Self-Contained Lighting Devices: System Evaluation and Applications

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Hazardous conditions, accidents, emergencies, temporary route changes and low visibility highway situations, among others, have prompted the nonflammable switchable light source which is mouldable to a low profile and a potentially long shelf life. Few systems can even theoretically fulfill such requirements. Radioluminescent devices are relatively expensive and difficult to encapsulate safely. Although long-lived they require high levels of radioactivity to produce bright light. For highway applications, a retroreflector recessed in the highway may fill the need as long as surface water does not interfere and where only straight ahead visibility is required. Unexpected curves or temporary changes in lane direction, however, demand another solution. Outside highway applications in fact, retroreflectors are of less use since such a bright directed source as headlights are rarely available and emergency light markers are needed for visibility or direction finding in such unlit circumstances as fires, rescue operations, emergency repair operations, etc. In these cases an inexpensive, switchable, nonflammable light source or marker is of utmost utility.

The recent development of a water-activated oxalate chemiluminescent system, as described in this report, is a very significant step toward the realization of a system which might fulfill all of the requirements outlined above and affords flexibility and potentials unique to this class of systems. The following discussion addresses the problem of wet nighttime roadway lane delineation as a specific case in the general range of problems arising from emergency hazardous or temporary situation visibility. In many ways the highways application is extremely demanding - road wear, surface temperatures, salt and oil, distances for effective visibility, lifetime without reapplication, low profile, and, of course, stringent cost-effectiveness. From this treatment of the system we hope the potential uses of chemiluminescent markers and lighting devices become evident.

In general, the factors that determine the properties required of a light source are peculiar to the problem to be solved. In the case of wet night roadway visibility the primary problem is driving lane delineation, which is adequately solved in daylight by painted stripes and occasional raised markers in roadway direction. On a dry night the retroreflective properties of the stripe allow for visibility of those

portions of paint struck by the motorists headlights to be seen readily, whereas stripes not within the beam are poorly seen. While this property minimizes the potential distraction of bright stripes nearby the passing motorist, those markers not in the path of his headlights are nearly visible - such as on a curve. This has become an increasing problem on multi-lane highways with raised center lanes and side guard-rails. It becomes a dangerous problem when lanes must be changed for construction or other emergency and where the previous lines often confuse the motorist at night. Raised retroreflectors are not effective in such situations since the driver's eyes are trained to follow the lane stripes.

The raised retroreflector solution to the wet night visibility problem is limited due to cost, high profile (snowplow damage) and directionality (not functional on curves).

In addition the shape of a raised marker placed at either end of a solid stripe is unfamiliar to most motorists. The major advantage seems to be fortuitous - the repeated bump of a tire striking the raised retroreflectors gives the motorist a nonvisual indication that he is crossing the lane. It can be argued that a different shape marker is valuable as an indicator of changing road direction, but the motorist seems to be already facing a complex enough visual situation in straight-line driving today. A better situation would be to have some uniform type of marking on straightaways and a change in shape for curves or other hazards. This is possible with the proposed self-luminous system.

The criteria for sufficient brightness and appropriate color have been discussed at length previously. Given sufficient edge contrast and the low background inherent in wet pavements at night, brightness levels of 0.1 to 0.5 foot lamberts (FtL) make a 6-inch wide 36-inch long stripe quite visible at 150 ft. An approaching motorist has the advantage of repeated marks to guide his eye and anticipate where the next mark will appear. Subjective tests of self-luminous markers will probably show that brightness levels of 0.05-0.1 FtL are more than adequate to locate the lane marker at 150 feet on the highway. Such levels of brightness would not be likely to distract the driver as he passes the markers close by. Brighter markers might, however, as stated above, on curves, exits and other unexpected lane changes. The color of objects seen at night at threshold intensities are seen as "white" regardless of the actual color. Therefore a green and yellow object seen side by side will both first appear to be white. If they are of equal brightness the green one will be seen about twice as easily as the yellow due to the scotopic (night or rod vision)

sensitivity of the eye which is maximum at 508-510 nm (green). Daylight vision peaks in the yellow at about 555 nm. It might be better to use a marker which is actually green so that it will be more visible. Yellow markers would then serve better in more dangerous areas such as curves.

The plight of the pedestrian, motorcyclist and bicyclist under rainy night conditions has not often been considered. Retroreflectors will not serve to help these individuals and self-luminous markers might be an answer. At accident locations where gasoline or other volatiles make flares and even electrical lighting dangerous a temporary coldlight marker would warn oncoming traffic.

A number of properties unique to chemically luminescent systems might prove useful in marker applications. The oxalate system is especially versatile in these regards. Light output can be triggered by the presence of water. This type of switch is useful not only in road visibility but also in many emergency situations: fire, rescue operations, etc. Since water is almost always available the output of oxalate can be made bright enough to read by - the commercial version maintains such levels for hours. The formulation probable will be cast in whatever shape and size necessary; from a thin paint-like film to the existing wand. The problem of field placement on such locations as a road surface should be no more difficult than for the preformed retroreflector stripes. In fact the system can probably be rejuvenated by reapplication of a top layer of chemical. In addition the system can be activated continously or quenched, given the proper chemical treatment. The most important factor in marker visibility is contrast. This factor can be enhanced by an appropriate increase in thickness or reactivity near the edge of the marker and a mask along the outside to create a high contrast edge. This factor is so important at threshold intensities that it outweighs the brightness factor. Retroreflectors cannot be so designed. An additional degree of flexibility is in color. Since the oxalate system color is dependent on the choice of a fluorescer, the color is subject to a degree of choice.

In conclusion, there are some basic differences between the active self-luminous and passive retroreflective type of marker. These differences become more pronounced when a variety of applications is considered. The cost effectiveness of the system is of course, likely to increase with use since the synthesis of chemicals will be limiting.

## APPENDIX II

### Linear Regression Analysis of Data From Table 1

Data in Table 1 were analyzed with a Hewlett-Packard H-P-65 programmable calculator using program "STAT 1-22A," linear regression.

Equations: $y = a_o + a_1 x$

where y is the chemiluminescence quantum yield, QY x $10^2$ and x is the sum of the Hammett sigma constants of the substituents.

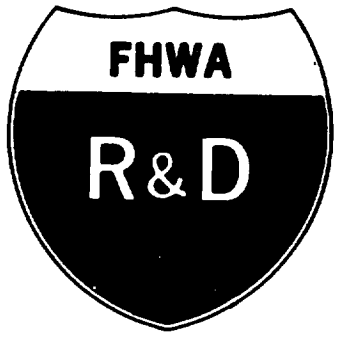
$$a_1 = \frac{\Sigma x_i y_i - \frac{\Sigma x_i \, \Sigma y_i}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}}$$

$$a_o = \bar{y} - a_1 \bar{x}$$

$$\bar{x} = \frac{\Sigma x_i}{n} \qquad y = \frac{\Sigma x_i}{n}$$

best fit:

$$y = -6.05 + 7.25\,x$$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